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CHEMICAL ACTION IN A MAGNETIC FIELD.

BY IRA REMSEN.

I.—*On the Deposition of Copper on Iron in a Magnetic Field.*

The question whether a metal in the magnetized condition differs in its chemical conduct from the same metal unmagnetized seems to be a fair one to ask, but, on first thought, the chances appear to be very much against obtaining a satisfactory answer. A difference in the *intensity* of the action of the metal in the two conditions would naturally be looked for first; but how can such a difference be detected in ordinary cases? Take the action of hydrochloric acid on iron for example. If a piece of iron be magnetized and treated with the acid, and the amount dissolved in a given time compared with the amount of a similar piece of unmagnetized iron dissolved under exactly the same circumstances, perhaps a difference might be detected. But the conditions are very complex, and it would be difficult to draw conclusions from experiments of this kind, particularly as the differences with which we would have to deal would probably be very minute. It is, further, possible that the total chemical action which takes place between hydrochloric acid and a piece of magnetized iron, on the one hand, and that which takes place between the same acid and a piece of unmagnetized

iron on the other, may be identical, while, at the same time, the action may be distributed differently in the two cases—in the one case taking place uniformly and in the other irregularly, being more intense in some places and less so in others. If this latter view be correct, and *a priori* it seems probable, then it should be possible to detect evidence of the influence of magnetism on chemical action. Taking again the case of iron and hydrochloric acid, if the action is irregular, then, after it has continued for some time, the iron itself should present the evidence of this fact in an irregularity of surface. Figures of some kind should be etched on the iron, and these would indicate the distribution of the action, as they would, of course, be deepest where the action is strongest, and, in general, the depth of the marks would be approximately proportional to the intensity of the chemical action.

Reasoning somewhat in the above manner, I was led a short time ago to undertake some experiments, the results of which are recorded in this paper. I have succeeded in showing, by means of a very simple experiment which any one may repeat in a short time, that magnetism does, in some way, as yet not understood, influence certain kinds of chemical action very markedly. Up to the present the experiments have been confined mainly to one particular case, that of the deposition of copper on magnetized iron. The results already reached in this case are so surprising and interesting that it appears to be desirable to put them on record at once, without waiting to take up other cases which will readily suggest themselves.

Experiments were first made on the action of dilute hydrochloric acid on thin iron sheets placed in thin glass vessels over the poles of magnets, but no satisfactory results were obtained. The iron used was as good thin sheet iron as I could get, but was very irregular in structure, and, if the magnetic condition of the iron had any influence on the action of the acid, the effects of this influence were so completely disguised by the structure of the iron as to escape detection. I have not yet given up the hope of obtaining results in this direction, but, in the meantime, a simpler method led unexpectedly to success, and I have temporarily abandoned the first line of experiments.

A shallow vessel of thin iron containing a solution of copper sulphate was placed on the poles of a permanent magnet of Jamin's construction capable of supporting twenty-five kilograms. In the course of one or two minutes the outlines of the poles could be

clearly seen through the solution. On pouring off the solution after allowing the action to continue for a time, the only result that could be seen was this: The copper was deposited in a fairly uniform way on the entire plate, except at the lines marking the outlines of the poles. These lines were sharply marked as depressions in the deposit, thus indicating that less action had taken place there. This experiment was repeated a number of times, the conditions being improved as much as possible. The only additional result obtained with the permanent magnet used was the development of lines other than those marking the poles, and much less regular. Between the poles, which are rectangular in shape, interrupted lines appeared parallel with the sides of the poles which were directed towards each other. These lines were produced by irregularities in the deposit of the copper. They appeared not only in the space between the poles, but at the ends of this space they curved outwards, and could be followed to the outer edges of the poles, and there showed a tendency to run parallel to those between the poles. The direction of these lines is shown in the accompanying lithographic plate Fig. 1. It will be seen that in general the direction is at right angles to the lines of force.

The result described naturally led to the inquiry whether, with a different shape and arrangement of the poles of the magnet, the copper would be deposited in similar irregular ridges at right angles to the lines of force, and a number of experiments have been performed to decide this point. First, a small electro-magnet with cylindrical poles 7 inches long by 1 inch in diameter and separated about 3 inches, was used. It was connected with a Bunsen dip-battery of six cells, such as is commonly used in chemical laboratories. The iron vessel and the copper sulphate solution were the same as those used in the experiments with the permanent magnet. The action in this case was very striking. Within half a minute the outlines of the poles were clearly visible. A space of about one sixteenth of an inch in width followed the circular form of each pole, and, as in the case first described, the development of this space was due to the fact that here no copper, or very little at least, was deposited, leaving the smooth surface of the iron practically in its original condition. On the parts of the iron included within these circles, that is, directly over the poles, there was a fairly uniform deposit. Outside of the circles, however, the most surprising effects were produced. The greatest amount of deposit was immediately adjoining the blank circles above referred to. From these places the copper

was deposited in irregular ridges, the general direction of which it was impossible to mistake. The ridges grew less and less distinct from the poles outward, and were finally lost, in the case under consideration, at about one and a half inches from the poles. These ridges are, as nearly as could be determined, at right angles to the lines of force, and consequently, *coincident with the lines marking the equipotential surfaces.* These ridges are not indistinct and difficult to recognize, but are very marked and their direction is unmistakable. An approximate representation of the appearance of one of the iron plates used in these experiments is given in Fig. 2, but the beauty of the phenomenon cannot be described nor represented.

A third form of the experiment was now tried. A large electromagnet, connected with a battery of twelve Bunsen's cells arranged in series, was used. The construction of the magnet is such that the poles are in the same line and the distance between them can be changed at will. The usual vessel with the solution of copper sulphate was placed in position on the poles, which were separated about two inches. Almost instantly the sharply defined outlines of the poles became visible, not a particle of copper being deposited upon these lines. Directly over the poles the deposit was nearly uniform as in the previous cases. Arranged over the whole plate except the portions just mentioned were again the remarkable ridges of copper, the direction of which changed gradually in passing from the edges of the plate nearest the poles towards the centre. At first they conformed nearly to the shape of the poles, but they became less and less curved the farther they were removed, until midway between the poles they were straight and at right angles to the line joining the poles. These lines were clearly developed within a minute from the time the action began, and could be seen distinctly through the solution. On first pouring off the solution the plate presented an appearance of striking beauty, the strongly marked ridges having the pure copper color, and the outlines of the poles being free from the deposit and retaining the original brightness of the iron. I have repeated this experiment a number of times in the presence of others, and it never fails to call forth the strongest expressions of pleasure, while I must confess that my own enthusiasm is aroused by it to an unusual extent. Fig. 3 shows at least the direction of the lines of deposit. It will here again be seen that they are at right angles to the lines of force, s was anticipated.

Although from the results already described the general direction of the lines of copper deposited can be predicted with a considerable degree of certainty for any given case, a final experiment was performed, with such an arrangement of the apparatus as to secure the strong magnetization of a point in the centre of the iron plate. The same magnet and battery were used as in the last experiment, but the magnet was so fixed in position that the line joining the two poles was perpendicular. Conical poles replaced those of truncated angular shape, and these were brought within about half an inch of each other. In this case the central point over the pole on which the vessel stood remained free from the deposit, while the ridges appeared in circles around this point, growing less and less strongly marked from the centre outward. These circles could be easily distinguished for a distance of nearly two inches from the pole—the largest circles thus having diameters of nearly four inches. Fig. 4 is intended to represent the appearance of the lines.

As a general result of these experiments it may be stated that *when copper is deposited from a solution of copper sulphate on a plate of iron in a magnetic field, it is arranged in ridges around the poles of the magnet, and in directions which are at right angles to the lines of force, and consequently, coincident with the lines marking the equipotential surfaces. Further, the outlines of the poles of the magnet are always sharply defined on the plate, as along these lines a portion of the iron of greater or less width is left unacted upon.*

It may be well here to give more specific directions in regard to the method of performing the experiments, in order to facilitate their repetition by others. The only difficulty is in the preparation of the iron plates. After many trials I have, for the present at least, found that plates can be most conveniently obtained in proper condition from ordinary ferrotype iron. Sheets of this may be obtained from any dealer in photographer's materials. The coating on the surface of the iron is removed by placing it in a bath of caustic soda for a short time, the process being hastened by heating. The plates, cut in sizes to suit the magnet to be used, are then bent up on all sides so as to form shallow vessels about a quarter to three-eighths of an inch in depth. To prevent rusting, it is better to leave the plates in the bath until they are needed. After a vessel is bent into proper shape it is washed

successively with water, a little ordinary concentrated hydrochloric acid, and again water. The bottom is dried, the vessel placed in position on the poles of the magnet, and the solution of copper sulphate poured in. The operations should be performed quickly, in order that the surface of the iron may be as bright as possible when the action begins. It should be observed, however, that the effects can be obtained distinctly without all these precautions, but for the best effects they are essential.

The plates appear best immediately after pouring off the solution. Then the copper has its proper color, and the parts of the iron which remain uncovered are bright; but very soon rusting begins, and before the plates are dry the color of the entire deposit, as well as of the unchanged iron, is that of the oxide of iron. All the original lines remain, however, fully as marked as at first. I have some plates which have remained for weeks unchanged, and which show the figures as clearly as on the day they were deposited. Of course, rubbing removes the deposit, so that, to be preserved, the plates should be protected in some way. I have tried photograph varnish, and this answers the purpose fairly well, though it causes the figures to appear less sharply defined than they do when uncovered.

Passing to a more important matter, we naturally ask, what is the cause of the phenomenon? In regard to this we can at present only speculate, and it is premature to speculate much on the subject as yet. There can be no doubt that the effects observed are to be ascribed to the action of magnetism, either on the iron plate or on the liquid, or on both. Experiment can decide between these possibilities. If the effect is due solely to magnetization of the iron, then non-magnetic metals will not exhibit similar phenomena; while, if it is due solely to the action of the magnet on the liquid, the same or similar effects should be obtainable with non-magnetic metals. The question thus left open will next occupy my attention. Whether, after all the facts are established which promise to be revealed in the course of the investigation thus begun, it will be possible to frame a satisfactory theory, remains to be seen. At all events, I propose to continue the study of the new set of phenomena.

In conclusion, it should be stated that a careful examination of the literature has failed to show that any experiments of the kind described in this paper have ever been performed. The only one I have found an account of which in any particular resembles mine is that of Jacobi.[1] This physicist desired to know whether iron

[1] Pogg. Annalen **149**, 341.

deposited by electrolysis in a magnetic field is itself magnetic. To determine this he arranged an apparatus thus: A candle covered with a thin, uniform layer of copper was placed in a cylinder containing a solution of an iron salt. The cylinder was then surrounded by a coil connected with a battery, and a current from another weak battery was passed through the iron solution, the copper cylinder forming the pole upon which the iron was deposited. After the action had continued for twenty-eight days the cylinder was removed, and it was found that the deposit was thicker at the ends than in the middle, but no *lines* of deposit were observed. It is questionable whether the action in this case is the same as that under consideration. I am inclined to think that the two are quite distinct phenomena, though it is possible that there is more resemblance than appears at first.

DETERMINATION OF CHROMIUM IN CHROME IRON ORE.

By H. N. Morse and W. C. Day.

When a determination of the chromium only is sought, the decomposition of chrome iron ore, according to our experience, can be best accomplished by fusing the material with potassium hydroxide in a wrought-iron crucible.

The method here described has, without exception, given us satisfactory results. From six to ten grams of potassium hydroxide are placed in a wrought-iron crucible (having the form of the ordinary porcelain crucible and a capacity of about 100 cc.) and gently heated until the evolution of steam ceases and the fused mass becomes tranquil. After cooling, the finely pulverized material, weighing not more than 0.5 gram, is placed upon the potassium hydroxide and evenly distributed over the surface. A flame just sufficient to thoroughly fuse the alkali is applied to the uncovered crucible, and the contents, as long as they remain in a fluid condition, frequently stirred with a piece of iron wire, which is allowed to remain in the crucible. The decomposition progresses rapidly, and the potassium hydroxide together with the soluble products of the decomposition soon begins to rise upon the sides of the crucible,

where it deposits itself in forms somewhat resembling the cauliflower. Within two or three hours the decomposition is complete, and the bottom of the crucible becomes dry. The crucible is then turned upon its side and the temperature of its under surface raised to a dull red heat. The incrustation on the interior of the crucible does not fuse at this temperature, but becomes rapidly yellow, owing to the oxidation of the chromium to chromate. At the end of two or three hours the oxidation is perfect. Portions of the incrustation retain a greenish color, however long the heating is continued ; but this is due to the presence of iron or manganese and not to unoxidized chromium.

After cooling, the crucible is placed in a porcelain evaporating dish and the contents removed by means of hot water. The solution, which at first has a greenish appearance owing to the presence of iron dissolved in the caustic potassa, is heated for some time in order to effect complete precipitation of the iron. The filtrate, which has a clear yellow color, is rendered slightly acid with pure dilute nitric acid, the aluminum precipitated with ammonia and washed by decantation. The chromate of potassium is then reduced and the silica rendered insoluble by evaporating to perfect dryness with an excess of hydrochloric acid. The residue is moistened with hydrochloric acid and treated with water.

It only remains to separate the chromium in the filtrate from magnesium and to determine it as chromic oxide. To do this we have preferred in each instance to first precipitate with barium carbonate.

We give here the data of twelve determinations upon material whose origin is unknown to us. Four of these (1–4) were made by ourselves, four (5–8) by Mr. A. G. Palmer, and the remainder (9–12) by Mr. W. S. Bayley, both students in this laboratory. The analyses reported were in each case made consecutively.

	Wt. of Ore taken.	Wt. of Cr_2O_3 found.	Percentage.
1.	0.3250	0.1343	41.32
2.	0.3465	0.1433	41.35
3.	0.3248	0.1343	41.36
4.	0.3383	0.1392	41.14
5.	0.2723	0.1120	41.12
6.	0.3955	0.1629	41.19
7.	0.3311	0.1358	41.02
8.	0.31285	0.1290	41.23
9.	0.3387	0.1392	41.10
10.	0.2995	0.1235	41.25
11.	0.3606	0.1478	41.00
12.	0.3007	0.1236	41.11

In order to assure ourselves that complete decomposition and oxidation had been effected, the same method of treatment was applied to the iron and aluminum precipitates as to the original material. This was done in the case of nine of the analyses here reported. But in no case was there any trace of chromium obtained from them. The average loss of the iron crucibles is about 0.2 gram. Much coarser material can be successfully analyzed by this than by the other methods in use. Its simplicity and economy also recommend it.

The only method on record, so far as we know, involving the use of potassium hydroxide for the decomposition of chrome iron ore, is that proposed by H. Schwarz,[1] who recommended fusion with potassium hydroxide in a silver crucible and addition of potassium chlorate to the fused mass. The decomposition by this method is doubtless easy and complete, but the rapidity with which the crucible is destroyed renders the method wholly impracticable.

JOHNS HOPKINS UNIVERSITY, *May* 1881.

Contributions from the Chemical Laboratory of Harvard College.

X.—ON FURFUROL AND CERTAIN OF ITS DERIVATIVES.

BY HENRY B. HILL.

[*Concluded from p.* 123.]

MUCOCHLORIC ACID.

Mucochloric acid was discovered in 1865 by Schmelz and Beilstein,[2] and since that time, as far as I know, it has never been further studied. The discoverers found its preparation so very laborious, and the yield which they obtained so small, that they made no extended investigation of it, but contented themselves with giving a short description of the acid, together with the analyses necessary to establish its composition. Although their account was certainly not encouraging, it seemed to me worth while to attempt its preparation, more especially in order to study the dichloracrylic

[1] Liebig's Annalen **69**, 212. [2] Ann. Chem. u. Pharm. Suppl. **3**, 280.

acid derived from it, and to compare this with the acid of the same composition which Wallach[1] had already made from chloralid. This investigation Mr. W. Z. Bennett undertook with me.

The method followed by Schmelz and Beilstein in making mucochloric acid was as follows: Pyromucic acid suspended in water was treated with chlorine at first in the cold and afterwards at boiling heat. When all action appeared to be over, the solution was somewhat concentrated on the water bath, and finally brought to crystallization by evaporation over sulphuric acid *in vacuo*. This method gave in our hands precisely the same discouraging quantitative results that Schmelz and Beilstein had obtained; and it was only after a long series of unsuccessful experiments that we succeeded in finding a simple modification of the method which enabled us to prepare material sufficient for investigation. We suspended the pyromucic acid in ten times its weight of water, cooled the whole well with ice, and passed in a rapid stream of chlorine until the liquid was thoroughly saturated. The temperature was carefully kept within a few degrees of the freezing point during this treatment with chlorine, and not unfrequently considerable quantities of the crystalline hydrate of chlorine separated. When the solution was saturated it was heated to boiling, after a few moments again cooled to 0°, and saturated once more with chlorine. When this operation had been repeated several times, crystals of mucochloric acid began to appear as the solution cooled. At first we filtered these crystals off, and subjected the filtrate to further treatment; but we found by experience that little or no product was gained after the sixth chlorination, and we, therefore, usually proceeded to this point before we removed the acid formed. We then collected the crystals which separated as the solution cooled, and evaporated the mother liquors on the water bath to the point of crystallization. The crystals were drained, pressed, and recrystallized from hot water. We further found it convenient to add to the pyromucic acid a small percentage of iodine. Although this was by no means essential, we found that our results were then more constant and the average yield greater. As the result of several preparations which we made in the course of the investigation, we obtained 129 grams of mucochloric acid from 202 grams of pyromucic acid. This corresponds to a little more than forty per cent. of the theoretical amount, as our average product, although

[1] Berichte der deutsch. chem. Gesellsch. **8**, 1580.

in single instances our yield has reached fifty per cent. The product made in this way crystallized from water in well-formed rhombic plates which in their properties agreed in every particular with the description of Schmelz and Beilstein. The acid melted at 125°, and was very soluble in alcohol or ether, sparingly soluble in cold water, readily in hot. Boiling benzol or chloroform dissolved it with readiness, while in carbonic disulphide or ligroin it was almost insoluble. The purity of our material was shown by the following analyses:

I. 0.7408 gram substance gave 0.7617 gram CO_2 and 0.0831 gram H_2O.

II. 0.5512 gram substance gave 0.5687 gram CO_2 and 0.0621 gram H_2O.

III. 0.2090 gram substance gave 0.3564 gram AgCl.

	Calculated for $C_4H_2Cl_2O_2$.	Found.		
		I.	II.	III.
C	28.40	28.06	28.13	...
H	1.18	1.25	1.25	...
Cl	42.01	...	...	42.16

Although mucochloric acid appears to form derivatives in some respects more stable and readily studied than the corresponding derivatives of mucobromic acid, we have thus far taken up more in detail only the dichloracrylic acid, which may easily be made from it by the action of alkalies.

Dichloracrylic Acid.

In 1877 Wallach[1] obtained a dichloracrylic acid as a product of the reduction of chloralid. This acid was afterward more carefully studied by Wallach and Hunäus,[2] and quite recently Wallach[3] has published a paper still further describing the acid and its salts, and correcting the work of Hunäus in several important particulars. At the time this investigation was begun this acid was the only disubstituted acrylic acid known, and, since its constitution was fairly established by the mode of its preparation, it seemed desirable to prepare the dichloracrylic acid from mucochloric, in order to compare the two acids.

[1] Berichte der deutsch. chem. Gesellsch. **8**, 1580.
[2] Berichte der deutsch. chem. Gesellsch. **10**, 567. Ann. Chem. u. Pharm. **193**, 19.
[3] Ann. Chem. u. Pharm. **203**, 83.

The decomposition of mucochloric acid into dichloracrylic and formic acids, under the influence of alkalies, is much more neatly accomplished than the corresponding reaction with mucobromic acid. Under ordinary conditions, but little hydrochloric acid is split off, and the yield of dichloracrylic acid is nearly 90 per cent. of that required by the equation,—

$$C_4H_2Cl_2O_3+H_2O=C_3H_2Cl_2O_2+CH_2O_2.$$

We never have noticed in the preparation of dichloracrylic acid either chlorpropiolic acid or any compound corresponding to that which brompropiolic acid forms with dibromacrylic. We usually have dissolved mucochloric acid in quite an excess of potassic hydrate, allowed the solution to stand for a short time, acidified with hydrochloric acid, and extracted with ether. The dichloracrylic acid left on evaporation of the ether may be purified by melting it several times with a little water. When dried over sulphuric acid it gave the following results on analysis:

I. 0.5280 gram substance gave 0.4894 gram CO_2 and 0.0720 gram H_2O.

II. 0.3670 gram substance gave 0.3399 gram CO_2 and 0.0477 gram H_2O.

III. 0.1037 gram substance gave 0.2123 gram AgCl.

IV. 0.2674 gram substance gave 0.5420 gram AgCl.

	Calculated for $C_3H_2Cl_2O_2$.	Found.			
		I.	II.	III.	IV.
C	25.54	25.28	25.25	...	...
H	1.42	1.51	1.45	...	...
Cl	50.36	...	...	50.62	50.10

This dichloracrylic acid forms small rhombic prisms which volatilize rapidly on exposure to the air. It is readily soluble in water, alcohol, ether, or chloroform, and it also dissolves freely in boiling benzol, carbonic disulphide, or ligroin. It melts at 85–86°, and, when solidified by quick cooling, melts again at the same temperature. The β dichloracrylic acid of Wallach, on the other hand, melts at 76–77° and its melting point falls to 63–64° when melted and suddenly cooled.

Argentic Dichloracrylate, $AgC_3HCl_2O_2$. The silver salt was precipitated in the form of fine felted needles on the addition of

argentic nitrate even to a dilute solution of the acid. The salt was quite stable and could be recrystallized from hot water without any marked decomposition.

I. 0.5460 gram substance gave 0.2808 gram CO_2 and 0.0299 gram H_2O.

II. 0.4819 gram substance gave 0.2494 gram CO_2 and 0.0253 gram H_2O.

III. 0.2511 gram substance gave, by Carius' method, 0.2910 gram AgCl.

IV. 0.2078 gram substance gave, by Carius' method, 0.2401 gram AgCl.

V. 0.2089 gram substance, precipitated by HCl, gave 0.1209 gram AgCl.

VI. 0.6768 gram substance, precipitated by HCl, gave 0.3909 gram AgCl.

Calculated for $AgC_3HCl_2O_2$.		Found.					
		I.	II.	III.	IV.	V.	VI.
C	14.52	14.03	14.12	...	...	...	...
H	0.40	0.60	0.58	...	...	...	...
Cl	28.63	...	...	28.65	28.56	...	...
Ag	43.54	...	...	...	...	43.55	43.49

Baric Dichloracrylate, $Ba(C_3HCl_2O_2)_2.H_2O$. The barium salt was prepared by neutralizing the aqueous solution of the acid with baric carbonate and concentrating the solution upon the water bath. On cooling, the salt separated in rhombic plates which were permanent in the air, and did not lose in weight over sulphuric acid *in vacuo*.

I. 0.2185 gram of the salt lost, when heated to 80°, 0.0088 gram H_2O, and gave, on ignition with H_2SO_4, 0.1174 gram $BaSO_4$.

II. 0.1941 gram of the salt gave, on ignition with H_2SO_4, 0.1041 gram $BaSO_4$.

III. 0.2402 gram of the salt gave, on ignition with H_2SO_4, 0.1281 gram $BaSO_4$.

IV. 0.9167 gram of the salt lost, when heated to 80°, 0.0395 gram H_2O.

Calculated for $Ba(C_3HCl_2O_2)_2.H_2O$.		Found.			
		I.	II.	III.	IV.
Ba	31.49	31.59	31.53	31.36	...
H_2O	4.14	4.03	...	...	4.31

For the further characterization of this salt we determined its solubility in cold water by the method of V. Meyer.

I. 5.6625 grams of an aqueous solution, saturated at 18°, gave, on evaporation and ignition with H_2SO_4, 0.1956 gram $BaSO_4$.

II. 2.416 grams of a solution, saturated at 18.5°, gave 0.0801 gram $BaSO_4$.

These determinations give as the percentages of the anhydrous salt contained in the solutions saturated at 18° and 18.5° respectively:

I.	II.
6.28	6.19

Calcic Dichloracrylate, $Ca(C_3HCl_2O_2)_2.3H_2O$. The calcium salt, which was extremely soluble in water, was made by neutralizing a solution of the acid with calcic carbonate. On cooling the concentrated solution, the salt separated in long, flat radiating needles, which were permanent in the air, but slowly effloresced over sulphuric acid.

I. 0.4077 gram of the air-dried salt lost, on heating to 95–100°, 0.0580 gram H_2O, and gave, on ignition with H_2SO_4, 0.1488 gram $CaSO_4$.

II. 0.6163 gram of the air-dried salt lost, on heating, 0.0875 gram H_2O.

III. 0.3217 gram of the dried salt (II.), corresponding to 0.3749 gram of the air-dried salt, gave, on ignition with H_2SO_4, 0.1348 gram $CaSO_4$.

Calculated for $Ca(C_3HCl_2O_2)_2.3H_2O$.		Found.		
		I.	II.	III.
Ca	10.69	10.73	...	10.58
H_2O	14.43	14.23	14.20	...

Potassic Dichloracrylate, $KC_3HCl_2O_2$. The potassium salt crystallizes from a solution of mucochloric acid in an excess of potassic hydrate (1 : 4) when this is strongly cooled. Although it is quite soluble even in cold water, it may readily be purified by recrystallization from hot water. From concentrated solutions it crystallizes on cooling in long, slender needles, which are anhydrous.

I. 0.3054 gram of the salt gave, on ignition and evaporation with HCl, 0.1283 gram KCl.

II. 0.2159 gram of the salt gave 0.0908 gram KCl.

	Calculated for $KC_3HCl_2O_2$.	Found. I.	II.
K	21.84	22.03	22.06

The foregoing results seemed to us to show with sufficient precision that our acid was essentially different from the β dichloracrylic acid of Wallach, since the two acids differed markedly in their physical properties, and their salts were also quite dissimilar. Following the analyses of Hunäus, Wallach[1] had assigned to the barium salt of the β dichloracrylic acid the formula $Ba(C_3HCl_2O_2)_2.5H_2O$, and to the calcium salt the probable formula $Ca(C_3HCl_2O_2).1\frac{1}{2}H_2O$; while the corresponding salts of our acid we had found to have the formulæ $Ba(C_3HCl_2O_2)_2.H_2O$ and $Ca(C_3HClO_2)_2.3H_2O$. Although the potassium salt of neither acid contained water of crystallization, one crystallized in plates, the other in needles.

Quite recently Wallach[2] has published the results of several determinations made since the publication of a preliminary notice[3] of our dichloracrylic acid. These determinations show that the formulæ which had previously been assigned to the barium and calcium salts of his acid were incorrect, and that they probably each contained two molecules of water. To these determinations, however, Wallach would attach but little weight for the identification of the acid, although he considers the isomerism of the two dichloracrylic acids to be fully established.

"Ich möchte aber nach den gemachten Erfahrungen diesen Bestimungen vorläufig keinen besonderen Werth für die *Charakterisirung* der Dichloracrylsäure aus Chloralid beilegen. Man wird besser thun, sich dafür an die scharf bestimmbaren Eigenschaften der *gemessenen freien* Säure und allenfalls an die tafelförmige Ausbildung des wasserfreien Kalisalzes, sowie an die angegebenen krystallographischen Daten des Baryumsalzes, anstatt an die bisher ausgeführten Wasserbestimmungen zu halten; für letztere müssen noch weitere Versuche vorbehalten bleiben. Jedenfalls muss aber der Zweck der obigen Angaben jetzt schon als erreicht bezeichnet werden: nämlich die völlige *Verschiedenheit der Dichloracrylsäure aus Chloralid* der nur die Formel $CCl_2=CH-CO_2H$ zukom-

[1]Ann. Chem. u. Pharm. **193**, 23. [2]Ibid. **203**, 83.
[3]Berichte der deutsch. chem. Gesellsch. **12**, 655.

men kann, *von der*, welche Bennett und Hill *aus Mucochlorsäure erhielten definitiv zu bestätigen.*"[1]

Unfortunately we have as yet been unable to obtain either our acid or its barium salt in a form which would admit of crystallographic study. Still, the differences already established leave no reasonable doubt that the two acids are isomeric, and the acid from mucochloric acid may therefore be distinguished for convenience as the α dichloracrylic acid.

The behavior of this acid towards reagents has thus far been little examined. On boiling with an excess of baric hydrate, it is decomposed in essentially the same way as the dibromacrylic acid, baric malonate being formed in abundance. This decomposition with alkalies we have not followed further, since it was evident that chlorpropiolic acid should be the intermediate product formed; and we wished not to interfere with the researches which Wallach had already undertaken with Bischof,[2] concerning the decomposition of β dichloracrylic acid by alkalies.

Although the acid does not take up bromine when heated with it to 100° in chloroform solution, it readily forms an addition product when heated for some time with undiluted bromine at 100°. The dichlordibrompropionic acid which is thus formed is at present under investigation in this laboratory.

Substituted Acrylic Acids from Brompropiolic Acid.

Mr. C. F. Mabery has studied with me some of the substituted acrylic acids which may readily be made by the addition of halogens or haloid acids to brompropiolic acid.

Dibromacrylic Acid of Fittig and Petri.

Brompropiolic acid dissolves easily in concentrated hydrobromic acid (b. pt. 126°), and, on standing for a short time, the solution deposits abundant crystals of a dibromacrylic acid, which is identical with that described by Fittig and Petri as resulting from the decomposition of tribromsuccinic acid. This acid may also be prepared to advantage from the solution of baric brompropiolate and baric bromide, which is obtained in the preparation of baric dibromacrylate by the action of baric hydrate upon mucobromic acid. It

[1] Loc. cit. 86.

[2] Berichte der deutsch. chem. Gesellsch. **11**, 751; **12**, 57.

is only necessary to precipitate the barium with dilute sulphuric acid, and to concentrate the solution upon the water bath. The acid which separates as the solution cools is easily purified by recrystallization.

From a hot concentrated solution the acid falls at first as an oil, but, after the solution has cooled somewhat, it separates in pearly scales, which melt at 85–86°. In analysis they gave the required percentage of bromine.

0.2614 gram of substance gave 0.4283 gram AgBr.

	Calculated for $C_3H_2Br_2O_2$.	Found.
Br	69.57	69.72

The solubility of the acid in water at ordinary temperatures we determined by neutralizing with baric carbonate the solution made according to V. Meyer's method, and evaporating the filtered solution with sulphuric acid.

I. 12.5364 grams of a solution, saturated at 20°, gave 0.2070 gram $BaSO_4$.

II. 11.6241 grams of a solution, saturated at 20°, gave 0.1712 gram $BaSO_4$.

III. 8.4358 grams of a solution, saturated at 20°, gave 0.1248 gram $BaSO_4$.

IV. 10.6740 grams of a solution, saturated at 20°, gave 0.1581 gram $BaSO_4$.

As the result of these determinations, we find that an aqueous solution of the acid, saturated at 20°, contains the following percentages:

I.	II.	III.	IV.
3.16	2.91	2.92	2.93

Fittig and Petri found that the dibromacrylic acid made from tribromsuccinic gave at 20° a solution which contained 3.355 per cent. of the acid.

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.2H_2O$. An aqueous solution of the acid was neutralized with baric carbonate, and the filtered solution evaporated on the water bath. On cooling the barium salt crystallized in rectangular plates, whose angles were, however, often more or less modified.

The air-dried salt lost, on heating to 100°, two molecules of water.

I. 1.4018 gram of air-dried salt lost at 100° 0.0226 gram H_2O.

II. 0.4644 gram of air-dried salt lost at 100° 0.0261 gram H_2O.

III. 0.5086 gram of air-dried salt lost at 100° 0.0299 gram H_2O.

Calculated for $Ba(C_3HBr_2O_2)_2.2H_2O$.		Found.		
		I.	II.	III.
H_2O	5.71	5.62	5.62	5.88

The anhydrous salt then gave:

I. 0.3425 gram of substance, dried at 100°, gave, on ignition, 0.1353 gram $BaSO_4$.

II. 0.4383 gram of the salt, dried at 100°, gave 0.1723 gram $BaSO_4$.

III. 0.2934 gram of the salt, dried at 100°, gave 0.1153 gram $BaSO_4$.

Calculated for $Ba(C_3HBr_2O_2)_2$.		Found.		
		I.	II.	III.
Ba	23.03	23.23	23.11	23.10

Fittig and Petri found in two determinations of water in the barium salt of their acid a somewhat higher percentage (6.73 and 7.27), and therefore assign it the formula $Ba(C_3HBr_2O_2)_2.2\frac{1}{2}H_2O$—(calculated 7.03 per cent.)

The solubility of the salt we determined by V. Meyer's method.

I. 3.9749 grams of a solution, saturated at 23°, gave, on evaporation with H_2SO_4 and ignition, 0.1748 gram $BaSO_4$.

II. 3.9148 grams of a solution, saturated at 20°, gave 0.1719 gram $BaSO_4$.

According to these determinations, the aqueous solution, saturated at 20°, contained the following percentages of the anhydrous salt:

I.	II.
11.23	11.21

Calcic Dibromacrylate $Ca(C_3HBr_2O_2)_2.3\frac{1}{2}H_2O$. The calcium salt we prepared by neutralizing a solution of the acid with calcic carbonate. On cooling the concentrated solution, the salt separated in long, radiating needles.

I. 0.5625 gram of the air-dried salt lost, when heated to 10°, 0.0668 gram H_2O, and gave, when ignited with H_2SO_4, 0.1356 gram $CaSO_4$.

II. 0.3460 gram of the salt lost at 100° 0.0394 gram H_2O and gave 0.0850 gram $CaSO_4$.

Calculated for $Ca(C_3HBr_2O_2)_2 \cdot 3\frac{1}{2}H_2O$.		Found. I.	II.
Ca	7.13	7.09	7.22
H_2O	11.23	11.88	11.39

Fittig and Petri found in two determinations of water, in the calcium salt of their acid, the percentages 11.56 and 11.47, from which they calculate the formula with $3\frac{1}{2}$ molecules of water, given above.

The physical properties of the acid and the analyses of the barium and calcium salts leave no doubt of the identity of this dibromacrylic acid with that described by Fittig and Petri, although our results differ slightly in some respects from theirs. The acid from tribromsuccinic acid we have made only in sufficient quantity to assure ourselves that no qualitative differences are to be detected in the properties of the two acids, or in the habit of several of their salts.

Iodbromacrylic Acid.

Brompropiolic acid dissolves readily in concentrated hydriodic acid (b. pt. 127°), and so rapid is the action that in a few moments the solution is filled with crystals of the addition product. The crude acid is pressed between folds of filter paper and recrystallized from hot water.

The acid separates from a hot, concentrated solution as an oil, but at a lower temperature it crystallizes in pearly scales, which melt at 110°. The acid is readily soluble in alcohol, ether or chloroform, but sparingly in benzol, carbonic disulphide, or ligroin.

I. 0.3800 gram substance gave 0.1828 gram CO_2 and 0.0307 gram H_2O.

II. 0.2945 gram substance gave 0.4480 gram AgBr+AgI.

	Calculated for $C_3H_2BrIO_2$.	Found. I.	II.
C	12.99	13.12	...
H	0.70	0.90	...
Br } I }	74.73	...	74.47

The solubility of the acid in cold water we determined by neutralizing the saturated aqueous solution, made according to the method of V. Meyer, with baric carbonate, and evaporating with sulphuric acid.

I. 11.1382 grams of a solution, saturated at 20°, gave 0.0785 gram $BaSO_4$.

II. 10.8923 grams of a solution, saturated at 20°, gave 0.0783 gram $BaSO_4$.

According to these determinations, the aqueous solution of the acid, saturated at 20°, contained the following percentages:

I.	II.
1.68	1.71.

For the further characterization of the acid, we prepared the barium, calcium and silver salts.

Baric Iodbromacrylate, $Ba(C_3HBrIO_2)_2.3H_2O$. The barium salt we made by saturating the aqueous solution of the acid with baric carbonate and concentrating on the water bath. From concentrated solutions it crystallizes in fine needles; from more dilute in rectangular plates. The air-dried salt contains three molecules of water, which it loses *in vacuo* over sulphuric acid.

I. 0.4660 gram of air-dried salt lost *in vacuo* over H_2SO_4 0.0360 gram H_2O, and lost then nothing at 80°.

II. 0.2832 gram of air-dried salt lost *in vacuo* over H_2SO_4 0.0208 gram H_2O, and afterwards, when heated to 80°, 0.0011 gram.

	Calculated for $Ba(C_3HBrIO_2)_2.3H_2O$.	Found. I.	Found. II.
H_2O	7.27	7.73	7.35

0.4427 gram of the dried salt gave, on ignition with H_2SO_4, 0.1498 gram $BaSO_4$.

	Calculated for $Ba(C_3HBrIO_2)_2$.	Found.
Ba	19.88	19.90

The solubility of the salt in cold water we also determined.

I. 2.0636 grams of a solution saturated at 20° gave, on evaporation with H_2SO_4, 0.0967 gram $BaSO_4$.

II. 3.0991 grams of a solution saturated at 20° gave 0.1457 gram $BaSO_4$.

From these determinations it follows that the aqueous solution, saturated at 20°, contains the following percentages of the anhydrous salt:

I.	II.
13.86	13.90

Calcic Iodbromacrylate, $Ca(C_3HBrIO_2)_2.3\frac{1}{2}H_2O$. The calcium salt resembles the barium salt closely in appearance, but is more soluble in water. The air-dried salt loses its crystal water completely *in vacuo* over sulphuric acid, or when heated to 80°.

I. 0.7622 gram of the air-dried salt lost 0.0771 gram H_2O at 80°.

II. 0.7172 gram of the air-dried salt lost 0.0698 gram H_2O at 80°.

	Calculated for $Ca(C_3HBrIO_2)_2.3\frac{1}{2}H_2O$.	Found.	
		I.	II.
H_2O	9.89	10.12	9.73

0.6518 gram of the salt dried *in vacuo* gave, on ignition with H_2SO_4, 0.1465 gram $CaSO_4$.

	Calculated for $Ca(C_3HBrIO_2)_2$.	Found.
Ca	6.76	6.61

Argentic Iodbromacrylate, AgC_3HBrIO_2. The silver salt was precipitated from an aqueous solution of the acid by the addition of argentic nitrate. It formed short, clustered needles, which could be recrystallized from water, with but little decomposition.

I. 0.4509 gram of substance gave 0.1597 gram AgCl and 0.0063 gram metallic silver.

II. 0.7458 gram substance gave, on precipitation with HBr, 0.3635 gram AgBr.

	Calculated for AgC_3HBrIO_2.	Found.	
		I.	II.
Ag	28.13	28.05	27.99

With hydrochloric acid, the addition takes place much more slowly; still, after long standing, the chlorbromacrylic acid is formed.

Of the products formed by the addition of halogens to bromopropiolic acid, we have thus far examined in detail only the tribromacrylic, although we have also made the diiodbromacrylic by the addition of iodine.

Tribromacrylic Acid.

Tribromacrylic acid may easily be made by adding slowly a slight excess of bromine to an aqueous solution of bromopropiolic acid. The color of the bromine gradually disappears, and the product of the reaction separates partially in the form of an oil. This oil gradually solidifies, and more of the same product can be extracted with ether from the aqueous solution. The resulting solid must be well pressed out, and may then be recrystallized from chloroform, or, better, from benzol. Thus prepared, it forms colorless, oblique prisms, which are very soluble in ether or alcohol, less soluble in cold chloroform or benzol, readily in hot, and soluble in carbonic disulphide or ligroin. It is but sparingly soluble even in boiling water. Melting point, 118°.

I. 0.3449 gram of the acid gave 0.1428 gram CO_2 and 0.0183 gram H_2O.

II. 0.1782 gram substance gave 0.3229 gram AgBr.

III. 0.1433 gram substance gave 0.2625 gram AgBr.

	Calculated for $C_3HBr_3O_2$.	Found.		
		I.	II.	III.
C	11.65	11.29	...	...
H	0.32	0.59		
Br	77.67	...	77.13	77.94

The acid when boiled with an excess of baric hydrate is hardly affected, although it is slowly decomposed by a boiling alcoholic solution of potassic hydrate. We have as yet isolated no products of this decomposition.

The solubility of the acid in water at ordinary temperatures we have also determined by the method of V. Meyer.

I. 11.4429 grams of a solution, saturated at 20°, gave, after neutralization with $BaCO_3$ and evaporation with H_2SO_4, 0.0597 gram $BaSO_4$.

II. 12.7846 grams of a solution, saturated at 20°, gave 0.0643 gram $BaSO_4$.

According to these determinations, the aqueous solution of the acid saturated at 20° contains the following percentages:

I.	II.
1.38	1.33

Baric Tribromacrylate, $BaC_3Br_3O_2.3H_2O$. The barium salt we made by neutralizing the acid with a solution of baric hydrate. On cooling the concentrated solution, it crystallizes in long needles, which effloresce over sulphuric acid.

I. 0.7888 gram of the air-dried salt lost over H_2SO_4 0.0532 gram H_2O.

II. 0.7585 gram of the air-dried salt lost *in vacuo* over H_2SO_4 0.0506 gram H_2O.

III. 0.4900 gram of the air-dried salt lost at 80° 0.0324 gram H_2O.

IV. 0.7024 gram of the anhydrous salt gave, on ignition with H_2SO_4, 0.2185 gram $BaSO_4$.

V. 0.4486 gram of the anhydrous salt gave 0.1398 gram $BaSO_4$.

Calculated for $Ba(C_3Br_3O_2)_2.3H_2O$.		Found.		
		I.	II.	III.
H_2O	6.68	6.75	6.67	6.61

Calculated for $Ba(C_3Br_3O_2)_2$.		Found.	
		IV.	V.
Ba	18.20	18.29	18.32

The solubility of this salt in cold water was determined by the method of V. Meyer.

I. 3.2130 grams of a solution saturated at 20° left, on evaporation with H_2SO_4 and ignition, 0.2349 gram $BaSO_4$.

II. 2.9600 grams of a solution saturated at 20° gave 0.2170 gram $BaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt:

I.	II.
23.62	23.69

Calcic Tribromacrylate $Ca(C_3Br_3O_2)_2.H_2O$. The calcium salt was made by warming the acid with water and calcic carbonate. It crystallized in needles which were permanent in the air, but lost in weight over sulphuric acid.

I. 0.4924 gram of the air-dried salt lost at 80° 0.0099 gram H_2O.

II. 0.8678 gram of the air-dried salt lost at 80° 0.0248 gram H_2O.

III. 0.4794 gram of the anhydrous salt gave, on ignition with H_2SO_4, 0.1001 gram $CaSO_4$.

IV. 0.8266 gram of the anhydrous salt gave, on ignition with H_2SO_4, 0.1707 gram $CaSO_4$.

Calculated for $Ca(C_3Br_3O_2)_2.H_2O$.		Found. I.	II.
H_2O	2.67	2.01	2.86

Calculated for $Ca(C_3Br_3O_2)_2$.		Found. III.	IV.
Ca	6.10	6.14	6.07

Argentic Tribromacrylate, $AgC_3Br_3O_2$. The silver salt is precipitated when argentic nitrate is added to an aqueous solution of the acid, but is more readily prepared from a solution of the acid in diluted alcohol. The salt is tolerably stable, and crystallizes in small, six-sided plates.

0.5267 gram of the salt gave 0.1848 gram AgCl.

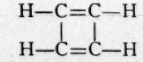
Calculated for $AgC_3Br_3O_2$.		Found.
Ag	25.96	26.40

Mr. Mabery has undertaken the study of the chlorbromacrylic and diiodbromacrylic acid, and will present the results of these investigations in a separate paper.

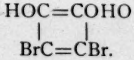
Theoretical Considerations.

Schmelz and Beilstein,[1] from a comparison of the formula of mellitic acid, $C_4H_2O_4$ (as it was then written), with that of mucobromic acid, $C_4H_2Br_2O_3$, were led to suspect a close connection between the two; but their investigations undertaken with the hope of proving this point yielded negative results.

In 1869, Limpricht[2] suggested that a series of compounds, among which were furfurol and its derivatives, contained a ring of four carbon atoms, and that they were therefore derived from an hypothetical hydrocarbon,—



just as the various compounds of the aromatic series were derived from benzol. As the formula which naturally suggested itself for mucobromic acid he gives,—



[1] Ann. chem. u. Pharm. Suppl. **3**, 280. [2] Berichte der deutsch. chem. Gesellsch. **2**, 212.

although I am at a loss to know precisely how this formula is to be interpreted. This hypothesis received temporary support from the discovery of the so-called tetraphenol by Limpricht and Rohde;[1] but further experiments made in Limpricht's laboratory failed to sustain it, and in the subsequent detailed account of these investigations[2] no allusion is made to it. In this paper Limpricht described the formation of fumaric acid by the action of bromine and water upon pyromucic acid, as well as the substance $C_4H_4O_3$, which he called fumaric acid aldehyde, and regarded as the product from which mucobromic acid was derived by substitution. In 1877 Baeyer[3] showed that this latter substance was in fact the half-aldehyde of fumaric acid, in that it could be converted into fumaric acid by the action of argentic oxide. At the same time he pointed out the difficulty of supposing that mucobromic acid, which empirically was a substitution-product from this aldehyde, could be formed from it by the direct action of bromine.

In 1878 Wallach and Bischoff[4] published a paper upon the action of alkalies upon the β dichloracrylic acid, which Wallach[5] had previously made by the reduction of chloralid. In a subsequent paper[6] upon the same subject they assumed that the structure of the dibromacrylic acid from mucobromic, which O. R. Jackson and I[7] had shortly before described in a preliminary notice, was established quite surely by its ready conversion into malonic acid, and Wallach was therefore led to append a note containing a suggestion which he had previously made, that the constitution of mucobromic acid was probably represented by the formula—

$$CBr_2{=}CH{-}CO{-}COOH.$$

In 1879 Toennies,[8] in investigating the action of bromine upon dibrompyromucic acid[9] in Baeyer's laboratory, found that a substance, $C_4H_2Br_2O_2$, was formed according to the equation—

$$C_5H_2Br_2O_3+Br_2+H_2O=C_4H_2Br_2O_2+CO_2+2HBr,$$

and that this could readily be converted into mucobromic by oxidation. This mode of formation led Toennies to the conclusion that mucobromic acid was the half-aldehyde of dibromfumaric acid.

[1] Berichte der deutsch. chem. Gesellsch. **3**, 90.
[2] Ann. Chem. u. Pharm. **165**, 278.
[3] Berichte der deutsch. chem. Gesellsch. **10**, 1362.
[4] Ibid. **11**, 751.
[5] Ibid. **8**, 1580.
[6] Ibid. **12**, 57.
[7] Ibid. **11** 1671.
[8] Ibid. **12**, 1202.
[9] Ibid. **11**, 1088.

Further investigation in this direction Toennies relinquished, in order to avoid interference with my work.

At the time of the publication of this paper by Toennies my own experiments had shown that this view was in part correct. The conversion of mucobromic acid by the action of argentic oxide or other oxidizing agents into the dibrommaleic acid of Kekulé showed with sufficient precision that it was the half-aldehyde of this acid. On the other hand, it was evident that the dibrommaleic acid itself did not belong to the fumaric series, as could fairly be inferred from its mode of preparation; but that it was in reality a substituted maleic acid, since it could be carried unchanged through its anhydride.

A more direct proof of this fact was furnished by the discovery by Bandrowski[1] of an isomeric acid of higher melting point, which could be converted into this by distillation.

Although it cannot be said that the constitution of fumaric and maleic acids is definitely established, the brilliant researches recently published from Fittig's laboratory leave but little doubt that the formula of maleic acid is—

$$\begin{array}{l} CH_2\text{—}COOH \\ | \\ =C\text{—}COOH. \end{array}$$

If this view of its structure be adopted, the structure of mucobromic acid must be represented by one of the formulæ—

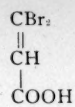
$$\begin{array}{l} CBr_2\text{—}CHO \\ | \\ =C\text{—}COOH \end{array} \qquad \begin{array}{l} CBr_2\text{—}COOH \\ | \\ =C\text{—}CHO \end{array}$$

The ease with which it is decomposed, even in the cold, by alkalies and the aldehyde group thus converted into formic acid, would possibly incline one to adopt the first of these formulæ.

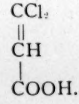
Unfortunately, no independent evidence concerning the position of the bromine atoms can as yet be drawn from the constitution of the dibromacrylic acid, which is formed at the same time, since

[1] Ibid. **12**, 1232.

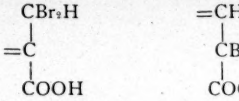
none of its reactions give a clew to its structure. It may only be asserted, with tolerable certainty, that its formula is not—



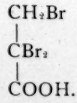
since the corresponding chlorinated acid made from mucochloric acid appears to be essentially different from the dichloracrylic acid of Wallach, and the formation of the latter from chloralid shows its formula to be—



If the structure of mucobromic acid is represented by one of the formulæ given above, it follows that the dibromacrylic acid obtained from it has one of the forms—



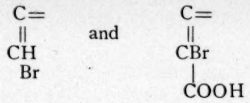
The formation of a tribrompropionic acid, melting at 116–117° by the addition of hydrobromic acid, would in itself be a sufficient reason for rejecting the second formula, if the structure of the tribrompropionic acid, melting at 92°, could be shown to be—



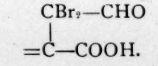
Although this is the constitution assigned to it by Michael and Norton,[1] it is evident that this formula is based upon a pure assumption concerning the structure of the α monobromacrylic acid from which it is made.

[1] This Journal, **2**, 18.

No more decisive arguments against the second formula can be drawn from the reactions or the derivatives of the dibromacrylic acid, although the formation of malonic acid follows more simply from the first formula, and the forms—



which the second formula renders necessary for bromacetylen and brompropiolic acids, seem hardly in its favor. It would therefore seem probable that the structure of mucobromic acid is—



The close connection between the disubstituted acrylic acids derived from mucobromic and mucochloric acids and maleic acid makes their further study extremely desirable, more especially in order to obtain additional evidence bearing upon the position of the halogen atoms. Investigations in this direction are now in progress in this laboratory.

IV.—DINITROPARADIBROMBENZOLS AND THEIR DERIVATIVES.[1]

By W. D. Schoonmaker and J. A. Van Mater.

In the second paper of this series a compound was described which was obtained by the nitrition of β-dinitroparabromanilidobenzol. This compound, β-dinitroparabromdinitroanilidobenzol, owing to the entrance of the two nitro-groups, became reactive toward alkalies, and, on treatment with sodic hydrate, the formation of a salt appeared to take place. The production of this compound in large quantities would, it was hoped, afford us an oppor-

[1]The former papers of this series, by P. T. Austen, were published in the Amer. Jour. Sci. and Arts, Aug. 1876, Feb. 1877, July 1878.

tunity of studying various interesting derivatives; for the easy substitution of the bromine atom would allow of the substitution of a large number of basic rests. As the preparation of the compound by treatment of the β-dinitroparadibrombenzol with aniline was very roundabout, owing to the difficulty of separating the β-compound from the other isomers, we concluded to try the effect of heating the β-dinitroparabromphenol with aniline, in the hope that the large number of negative groups present would render the hydroxyl capable of substitution by a positive residue. It also appeared probable that if this reaction did not take place, the bromine atom might be open to substitution.

A number of experiments were made in which the phenol was heated with aniline in a closed tube from one to five hours at 100° and 160°. The result, however, was negative. A reaction had taken place, but the nitro-groups seemed to have acted on the aniline, producing an uninviting tar. No evolution of ammonia was observed, so that the reaction is different from that of picric acid on aniline, whereby ammonia is copiously evolved.

In the hope of obtaining an amido derivative of the phenol, it was reduced with tin and hydrochloric acid. The reduction took place easily. On evaporating the colorless solution freed from tin by precipitation with hydrogen sulphide, it became rapidly colored, and a black pulverulent substance separated.

We were not able with the means at our control to so conduct the operation as to avoid the oxidation. The black substance was insoluble in alcohol, but dissolved in concentrated sulphuric acid with a superb blue color, and did not fuse at 250°. It is probably an azoxycompound. A careful examination of it will be carried out as soon as a sufficient quantity can be obtained.

β-Dinitroparabromphenetol, $C_6H_2(NO_2)_2BrOC_2H_5$.

Some pure phenol silver salt, made by boiling the phenol in alcoholic solution with silver nitrate and a slight excess of silver oxide, was boiled in a flask with a return condenser with ethyl iodide. The reaction took place easily, as was shown by the change from the brilliant red of the silver salt to the yellow of the silver iodide. The whole was evaporated to dryness on a water bath, and extracted with boiling dilute alcohol.

The substance purified by repeated crystallizations from alcohol, formed small, light needles of a pearly color, fusing at 66° (uncorr.),

very easily soluble in alcohol and hot water. It is decomposed in the cold by sodic hydrate solution with regeneration of phenol. An analysis gave:

	Calculated for $C_6H_3(NO_2)_2BrOC_2H_5$.	Found. I.	II.
Br	27.50	27.82	27.79

Atomic Migration in the Mononitroparadibrombenzol Molecule.

In nitrating paradibrombenzol with a mixture of sulphuric acid and the strongest fuming nitric acid, it was remarked by Dr. Austen that small amounts of other dinitro-compounds than the α, β and γ appeared. The most marked among these was a dinitro-compound with a fusing point of 120°.

The yield of the three isomers already described seemed also to vary with the time, degree of heat and strength of the acids. As but little is known in regard to the causes which determine the formation of several isomers at the same time, we concluded to experiment with nitrition mixtures of various strengths. Fifty grams of paradibrombenzol were nitrated by boiling for three hours with a mixture of 160 grams of fuming nitric acid of 1.41 sp. gr. and an equal volume of concentrated sulphuric acid. After nitrition the whole was poured into cold water, and the separated nitro-compound allowed to harden. The resulting cake was dissolved in dilute alcohol, and boiled with potassium nitrite to convert[1] the β-dinitroparadibrombenzol into potassium β-dinitroparabromphenylate. The whole was then evaporated nearly to dryness, to drive off the alcohol, after which the mass was thoroughly extracted with boiling water. In this manner the β-dinitroparadibrombenzol was entirely removed as potassium β-dinitroparabromphenylate, which is easily soluble in boiling water, while the other nitro-compounds were left as a cake at the bottom. The amount of β-dinitro-isomer formed was small. The cake was dissolved in carbon disulphide and allowed to crystallize. On standing, a heavy crop of crystals was obtained. These were purified by repeated crystallizations from alcohol. The substance thus obtained proved to be the known mononitroparadibrombenzol, fusing at 84°, and giving, on analysis,

	Calculated for $C_6H_3(NO_2)Br_2$.	Found.
Br	56.94	56.77

[1]See Am. J. Sci. **16**, 5.

We were unable to obtain even a trace of the α-dinitro-isomer. From this it would appear that with acids of a certain strength, only the β-dinitroparadibrombenzol is formed. Whether the α and γ isomers are subsequently produced from the β by atomic migration, or by direct nitrition from the original dibrombenzol, we cannot say. It would appear probable from the above, however, that in the nitrition with the strong acid, in which case the three isomers are produced, the three are not formed simultaneously, but that the β-compound is produced first. The mother-liquor of the crystallizations from carbon disulphide on evaporation yielded decreasing amounts of the above substance. The liquor was evaporated to dryness and kept for some time on a water-bath to expel all traces of the carbon disulphide. In this manner a yellow oil was obtained resembling the substance which has been considered as the γ-dinitroparadibrombenzol. Instead of reacting easily with alcoholic ammonia, however, it remained unacted upon after standing with it for a week. An analysis showed this oil to be a liquid mononitrodibrombenzol.

Calculated for $C_6H_3(NO_2)Br_2$.		Found.
Br	56.94	57.41

Several repetitions of the above experiments, substantially the same but varying in details of manipulation, gave the same results, viz. a small yield of β-dinitroparadibrombenzol, a large yield of mononitroparadibrombenzol, a considerable yield of the liquid mononitrodibrombenzol.

According to our present theory there can be but one mononitroparadibrombenzol, hence the liquid mononitrodibrombenzol which is produced must be formed by atomic migration. It was not clear, however, whether the mononitroparadibrombenzol was first formed and the liquid isomer from it by atomic migration, or whether a migration took place in the paradibrombenzol forming an isomeric dibrombenzol which then was nitrated.

To determine this, some pure mononitroparadibrombenzol was boiled with the nitrition mixture above described. The resulting product was extracted with potassium nitrite in the usual manner. Small amounts of the β-dinitro-compound had been formed. The residues were nitrated again, and extracted with potassium nitrite. This process was repeated three times. At each nitrition the mass left after extraction with the nitrite became softer, showing an

increase in the amount of oil. The unchanged monitroparadibrombenzol was then removed from the cake by crystallization from alcohol. The alcoholic mother-liquor gave on evaporation an oil which, on analysis, proved to be the isomeric mononitrodibrombenzol.

Calculated for $C_6H_3(NO_2)Br_2$.		Found.[1]	
		I.	II.
Br	56.94	57.65	57.29

This shows, then, that the atomic migration takes place *after* the introduction of the nitro-group.

We hope to be able to reduce the liquid mononitrodibrombenzol, and by splitting off the amido group from the resulting dibromaniline, to obtain the dibrombenzol of which it is a derivative. So far the reduction has not been successful. Tin and hydrochloric acid give a tar from which we have not been able to obtain any defined compound.

The liquid mononitrodibrombenzol is not affected by alcoholic ammonia under pressure at 100°. Some reaction takes place, however, at 160°.

To ascertain if the atomic migration was simply the effect of heat independent of the acid, some pure mononitroparadibrombenzol was heated at 250°–300° in capillary tubes dipping in sulphuric acid. The substance evaporated so rapidly that no observation could be made. Portions were then heated in small closed tubes in an air bath, but they exploded with great violence. To avoid this, combustion tube was used. About a gram was heated in a closed combustion tube about four inches long. As yet we have observed no indications of the formation of the oily isomer.

The above investigation was conducted under the direction of Prof. P. T. Austen.

RUTGERS COLLEGE, New Brunswick, N. J.

[1] Analyses of different nitritions.

ON THE MOLECULAR WEIGHT OF HYDROFLUORIC ACID.[1]

By Prof. J. W. Mallet, F. R. S.

The analogies of fluorine with the halogens on the one hand and with oxygen on the other have often been remarked upon. The general resemblance of fluorine compounds to the corresponding compounds of chlorine is manifest, and the two elements are usually classed together; but some striking differences force themselves upon the attention, such as those existing between the chloride and fluoride of calcium, chloride and fluoride of silver, etc., and the marked tendency of the fluorides to the formation of double salts with formulæ analogous to those of oxygen compounds, as well as the formation of many salts including both oxygen and fluorine, suggests some close natural relation between these elements themselves.

When the principle of quantivalence or atomicity first began to assume distinct shape, it became a matter of special interest to decide whether fluorine should be classed with chlorine amongst the monad elements, with the formula HF for hydrofluoric acid, and the atomic weight 19 for fluorine itself, or should be placed with oxygen amongst the dyads, writing H_2F for hydrofluoric acid, and assuming the atomic weight of fluorine as 38. For some time, although analogies were chiefly in favor of the former view, no direct evidence was available for the settlement of this question, but in 1869 it seemed to be supplied by the researches of Gore,[2] who, heating silver fluoride in contact with an equivalent quantity of pure and dry hydrogen, observed that "one volume of hydrogen in uniting with fluorine produces, not simply one volume of gaseous product, as it does when uniting with oxygen, but two volumes, as in the case of its union with chlorine." Further on, in the same paper, after giving his results as to the amount of silver in the fluoride used, he says: "These results, combined with the foregoing experiments on molecular volume, agree with the conclusion that a volume of hydrogen weighing 1 unites with 19 parts by weight of fluorine to form 2 volumes of hydrofluoric acid, and that

[1]The substance of this paper was verbally presented, by invitation, at the meeting of the National Academy of Sciences at Washington, April 22, 1881.

[2]Philosophical Transactions for 1869. A further paper, on silver fluoride, appeared in 1870.

the specific gravity of gaseous anhydrous hydrofluoric acid is ten times the amount of that of hydrogen."

Gore's experiments were made with somewhat small quantities of the materials used (about a gram of silver fluoride and 90 or 100 cubic centimetres of hydrogen), and in opaque vessels of platinum, the volume assumed by the gaseous hydrofluoric acid being ingeniously determined by raising or lowering the cylindrical platinum receiver, so that the level of the mercury in which it was placed remained the same inside and out, and reading off an external scale. The whole apparatus was heated in an air-bath to 93°–100°C. before making the final reading. It is stated that fourteen separate attempts were made to ascertain the volume of gaseous product formed, but the numerical results of only two of these are given. They seem fairly to establish the fact that at temperatures near 100° hydrofluoric acid exists as HF, 93.3 and 98.5 per cent. respectively of the theoretical volume being obtained after allowance for expansion at the temperature employed. The atomic weight of fluorine is thus established as 19, not 38.

Certain measurements of the gaseous acid are, however, given for lower temperatures, though far above the boiling point (67° F., as found by Gore himself=19.5° C.) which represent distinctly smaller volumes. Thus at 139° F. (59.5° C.) the volume was but 85.8 per cent. of that required by theory, and at 160° F. (71° C.) it was 88.1 per cent.

Hence it seemed still desirable to try to ascertain whether the acid exhibits a different but definite vapor density at a temperature nearer the boiling point, though high enough to preclude any actual liquid acid remaining, operating on quantities large enough to give decisive results with even rough weighings, and if possible in transparent or translucent vessels. With this object in view I have made the following experiments.

Perfectly pure Greenland cryolite, carefully selected in choice fragments, was pulverized in a clean iron mortar, heated to 300° C. for some time, and transferred while still warm to a well dried and warm bottle. Sulphuric acid was prepared of full strength by adding to a quantity of the purified acid of 95 or 96 per cent. a small excess of pure sulphur trioxide, and passing for several hours a well dried and gently warmed current of air through the liquid; this was also preserved in a well stoppered bottle until needed. The cryolite and acid were heated together in a leaden retort, the capital of

which was clamped on without lute, and the hydrofluoric acid vapor given off was conducted downwards through a worm of leaden tube, 6 mm. in interior diameter and 3.5 metres long, surrounded by crushed ice, into a leaden bottle cooled by a freezing mixture of ice and salt. The interior of all the leaden apparatus had been previously crusted over by passing hydrofluoric acid vapor through for some time. The joints were made by simply wrapping tightly with lead foil, and ligating with wire. The quantity of the materials used was such as to produce eight times the amount of hydrofluoric acid necessary to fill with vapor the leaden bottle and the flask and connecting tubes to be afterwards used, even assuming the highest vapor density that could well be expected.

The flask in which the vapor was to be weighed was of good Bohemian glass, and held nearly 4½ litres, being as large as could be well managed in the balance case. It was slung in a light network of platinum wire, with a suspending ring at top, and was, after thorough drying, carefully coated over the whole inside surface with clear, colorless paraffine,[1] poured in in the melted state, and evenly distributed by turning round and round the gently-warmed flask. The melting point of the paraffine was 56° C., well above the temperature to be afterwards applied. The neck of the flask was accurately fitted with a sound, soft cork, previously well dried and soaked in paraffine. Through this cork passed two glass tubes of about 5 mm. bore, one of which extended about two-thirds of the way to the bottom of the flask, and just above the cork was bent at right angles, the short projecting limb being some 20 mm. long. The other tube ended just below the cork on the inside of the flask, came out straight, and projected also about 20 mm. on the outside. Both were drawn down a little in diameter, about 5 mm. from the outside ends, so as to form a little socket for the small cork by which each tube was to be closed, insuring this cork coming to exactly the same position when inserted. The two small corks, the whole of the interior of the glass tubes, and so much of their exterior surface as was to be inside the flask were thoroughly protected by paraffine. The specific gravities of the glass, paraffine, platinum and paraffine-coated corks with tubes were taken at

[1]The dry acid in the gaseous state does not act upon glass, but, as it did not seem certain that, by the process used, perfect exclusion of moisture would be secured, it was thought better to take this precaution.

about the temperature to be used, and the figures obtained corrected for buoyancy in air by the formula—

$$G_r = G_a - \rho(G_a - 1)^1$$

From the thus corrected specific gravities, and careful weighings in air of observed temperature and pressure, the volumes and absolute weights *in vacuo* of all the materials concerned were deduced, save in the case of the hydrofluoric acid vapor itself, the volume of which was obtained by an actual calibration[2] of the part of the flask and tubes occupied by it.

As soon as the distillation of the acid and its collection in the leaden bottle was complete, the retort and capital were disconnected from the worm, and the upper end of the latter connected with the bent tube of the paraffine-lined flask, interposing in the first experiment another small flask, also protected by paraffine, and containing a little phosphorus pentoxide, as the means of removing any last traces of aqueous vapor. Removing the freezing mixture from about the leaden bottle, the latter was surrounded with water at 25° C., and the water surrounding the worm was brought to the same temperature, while the flask was at 1° or 2° lower. The hydrofluoric acid thus vaporized filled the whole apparatus, gradually expelling the air, and the excess escaped through a long India-rubber tube attached to the exit glass tube, and carried through a hole in the door-casing to the outside atmosphere, thus avoiding danger to the lungs and eyes, and risk of corrosion of the outside of the flask. When the escape of vapor slackened, the two tubes entering the flask were quickly disconnected from the rest of the apparatus and the little paraffine-soaked corks at once inserted. In doing this but one tube at a time was open, and that but for a moment.

The flask was then placed in a deep cylinder of sheet zinc, of diameter to just fit it, and this was immersed in a much larger cylinder, containing some 30 litres of water, at a little over 30° C., a cover with small openings in it being fitted over both. Previous experiment with a similar flask of air and enclosed thermometer

[1] G_r being the real specific gravity of the body, G_a the apparent specific gravity of same taken without air correction by simple weighings in air and water, and ρ the ratio of the densities of air and water under existing conditions of temperature and pressure.

[2] With water of known temperature, as the weight of mercury necessary would hardly have been safely borne by the flask.

showed what small allowance to make in the temperature of the water in order to bring the flask and its gaseous contents to the desired point. In the actual experiments with hydrofluoric acid a thermometer was placed on the upper part of the outside of the flask, while another was immersed in the water of the outer vessel. From time to time, as the temperature of the flask rose, the little cork was partly withdrawn for a moment from the straight vertical exit tube, and the surplus vapor was thus allowed to escape. In doing this one or two small, but bad, burns were made upon the fingers by the frightfully corrosive dry acid, of whose dangerous character one can hardly speak too strongly.

When the temperature of the flask had become stationary at or very close to 30° the little corks were firmly inserted in their seats, the flask was removed from the zinc cylinder, allowed to cool to the temperature of the balance-room, which had, however, been warmed up for several hours by a stove to a little over 25°, and was then accurately weighed.

The following result was obtained in the first experiment:

Weight of flask, etc., and vapor, *in vacuo*,	393.781	grams.
" " empty, "	386.531	"
Weight, *in vacuo*, of 4347.4 cc. of vapor at 29° C. and 743.7 mm. (cor.) = 3846 cc. at 0° C. and 760 mm.,	7.250	grams.
Hence, 1 liter of vapor at 0° and 760 mm. =	1.885	grams.
Hence, sp. gr. of vapor (H* = 1) =	21.06,	
or molecular weight =	42.12.	

As soon as the weighing was over the flask was washed out with distilled water enough to largely dilute the acid, into a platinum dish, and the purity of the liquid examined. It was quite clear and free from silicon or lead, and gave no reaction for sulphuric or sulphurous acid, but on testing with ammonium molybdate very distinct evidence was obtained of the presence of phosphoric acid. This had been suspected from the energy with which the phosphorus pentoxide, of which fortunately but little had been used, was attacked by the vapor. In all probability phosphorus pentafluoride had been formed and carried forward with the hydrofluoric acid. This may serve to account for the vapor density of the latter coming out somewhat too high for even the formula

*One liter of hydrogen at 0° and 760 mm. at Univ. of Va. = .089488 gram.

H_2F_2 (requiring sp. gr. = 20). Any traces of air or aqueous vapor which might have been present would, of course, have tended on the contrary to produce a lower result.

In order to avoid this ascertained source of error in a second experiment, the phosphorus pentoxide was omitted altogether, the upper end of the leaden worm was directly connected to the large flask, and as the means of finally drying the vapor, a little sulphuric acid of full strength (pure H_2SO_4—not SO_3) was added to the liquid hydrofluoric acid in the leaden bottle while it was still in the freezing mixture, before proceeding to vaporize the latter acid at the very moderate temperature of 25°. A new flask, lined with paraffine and fitted with tubes as before, was used, and the following result was obtained:

Weight of flask, etc., and vapor *in vacuo*, 428.255 grams.
" " empty " 421.436 "

Weight, *in vacuo*, of 4394.7 cc. of vapor at 30.5° C. and 745.2 mm. (cor.) = 3876.5 cc. at 0° C. and 760 mm., 6.819 grams.
Hence, 1 litre of vapor at 0° and 760 mm. = 1.759 gram.
Hence. sp. gr. of vapor (H = 1) = 19.66,
or molecular weight = 39.32.

In this case the dilute acid washed out from the flask after the experiment seemed to be quite pure, or at any rate was free from silicon, lead, sulphuric and sulphurous acids. In both experiments the flask was, immediately after weighing, carefully inspected in a strong light, and no visible trace of liquid could be observed on the inside surface.

The glass, examined after removal of the paraffine, was found quite uninjured, except a slight trace of corrosion on the outside close to the exit.

The figures obtained obviously justify the assumption that at 30° C. the molecule of hydrofluoric acid vapor should be represented not as HF, but as H_2F_2, since the agreement with this assumption of the vapor density obtained in the two experiments is too close to be fairly accounted for by the mere general idea of imperfect gaseous condition, and it is certain that no such quantity of actually liquid acid as would be necessary to account for the double weight could possibly have escaped detection on the inner surface of the flask. At higher temperatures, such as those at

which Gore's measurements were made, dissociation manifestly takes place, leading to the production of diatomic molecules of HF.

The structure of the molecule of double weight, H_2F_2, may be well viewed as resulting from fluorine behaving not only as a monad but also as a triad, and acting in double atoms,

$$-F = F-,$$

like those of nitrogen,

$$-N = N-$$

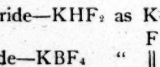
in the di-azo compounds. In such a condition the element presents a pseudo-dyad character, and becomes capable of replacing oxygen, and manifesting the *linking* function of the latter. Admitting, therefore, that the atomic weight of fluorine remains fixed at 19, we can see that the molecule of hydrofluoric acid may at high temperatures be H—F, analogous to that of hydrochloric acid, while at a little above the boiling point under ordinary pressure the structure may be H—F=F—H, and thus analogous to that of water.[1]

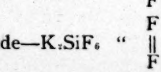
This assumption, supported by the experimental evidence now brought forward, serves conveniently to explain the constitution of a number of fluorine compounds, whose formulæ are difficult to write in a satisfactory way if fluorine be considered as exclusively monad.

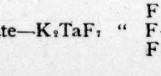
Thus we may view:

Potassium hydro-fluoride—KHF_2 as K—F=F—K

Potassium boro-fluoride—KBF_4 "

Potassium silico-fluoride—K_2SiF_6 "  *

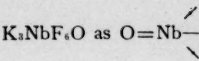
Potassium fluo-tantalate—K_2TaF_7 "  †

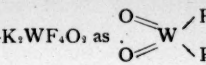
Potassium fluoxy-niobate—K_2NbF_5O as  †

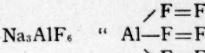
[1] Gore sums up the results of his numerous experiments on the chemical behavior of this interesting substance with the sentence: "From the various experiments already described, we may conclude that hydrofluoric acid is by its properties placed between hydrochloric acid and water, but is much more closely allied to the former than to the latter."

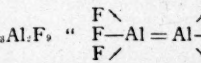
* On the type of a meta-silicate. Like formulæ apply to the analogous compounds of titanium, zirconium and tin.

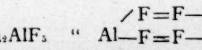
† Or these formulæ may be doubled, so as to correspond exactly with the oxygen pyro-tantalate and pyro-niobate.

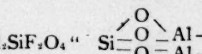
Potassium fluoxy-niobate (cuboid-Marignac) — K_3NbF_6O as  *

Potassium fluoxy-tungstate—$K_2WF_4O_2$ as  †

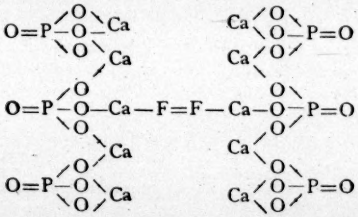
Cryolite Na_3AlF_6 " 

Chiolite $Na_5Al_3F_{14}$ " 

Chodneffite Na_2AlF_5 " 

Topaz $Al_2SiF_2O_4$ "  ‡

Apatite—$Ca_5P_3FO_{12}$—might be written:

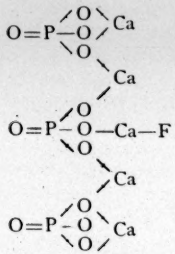


but, in view of the replacement of fluorine by chlorine in this mineral, as in the analogous pyromorphite and mimetite, it is doubtless better, as well as simpler, to suppose the molecule to be merely—

* On the type of an ortho-niobate.

† As for the normal tungstate. The case of the fluoxy-molybdate is of course the same.

‡ Like Andalusite—Al_2SiO_5—



UNIVERSITY OF VIRGINIA, *April* 26, 1881.

Laboratory Notes from the University of Cincinnati.

XX.—SOME DOUBLE AND TRIPLE OXALATES CONTAINING CHROMIUM.

BY F. W. CLARKE.

Chromic oxalate unites with other oxalates to form two well known series of double salts. One series is represented by the blue potassio-chromic oxalate, $Cr_2K_6C_{12}O_{24}6H_2O$. The other is typified by the red salt, $Cr_2K_2C_6O_{16}8H_2O$. The compounds described in this paper belong to the higher series.

The barium, strontium, and calcium salts of this series were discovered by Rees-Reece.[1] By mixing solutions of the ammonium salt with the chlorides of barium, strontium, and calcium, he obtained precipitates of dark violet silky needles, having the following formulæ:

1. $Cr_2Ba_3C_{12}O_{24}.12H_2O$.
2. $Cr_2Ba_3C_{12}O_{24}.18H_2O$.
3. $Cr_2Sr_3C_{12}G_{24}.18H_2O$.
4. $Cr_2Ca_3C_{12}O_{24}.36H_2O$.

By a different process, Berlin[2] prepared a calcium salt with 18 aq., a lead salt with 15 aq., and a silver salt with 9 aq.; besides other compounds which need no mention here.

[1]Compt. Rend. **21**, 1116. [2]Berzelius' Jahresbericht, **24**, 244.

About a year ago I requested Mr. E. A. Kebler to reprepare the barium salts described by Rees-Reece. The only variation from the method of the latter chemist was in using the potassium salt instead of the ammonium salt for the precipitant. Masses of very dark green silky needles were thrown down, and these were easily recrystallizable from boiling water. Two hydrates of the desired salt were thus obtained, one agreeing with the twelve molecule salt of Rees-Reece, while the other, lighter colored, contained but seven molecules of water. For the latter, the subjoined analytical data were found:

	Found.	Theory.
Cr	8.94	8.90
Ba	34.96	35.16
H_2O	10.91	10.77

The formation of this new hydrate naturally led to experiments aimed at the discovery of the conditions under which different degrees of hydration were produced. Although this point was not definitely settled, interesting results were secured. Four samples of the double oxalate were precipitated, two from dilute and two from concentrated solutions. Two were thrown down in the cold, and two were precipitated boiling. All the precipitates were in the form of green silky needles, which were carefully air dried. In these several preparations the following percentages of water were obtained:

Precip.	concent'd,	cold	9.50	9.78	9.19			Mean	9.49
"	"	hot	9.39	9.31				"	9.35
"	dilute,	cold	9.98	9.90	9.43	10.10	10.72	"	10.03
"	"	hot	12.07	12.13	11.12			"	11.77

Theory for 6 molecules of water 9.38
" " 7 " " 10.77
" " 8 " " 12.13

It will be seen that the two salts precipitated from concentrated solutions are definitely hexhydrated; the third salt gave doubtful results; while the last agrees fairly with the percentage for eight molecules of water. Evidently the six molecule salt is definite and typical; doubtless the twelve and eighteen molecule salts of Rees-Reece are definite also; all the other hydrates may be but mixtures of the lowest with one of the higher compounds. This point

remains to be settled. The color is always darker, the higher the hydration; but, though green under ordinary circumstances, all the salts described in this paper become dull violet by gaslight. Specific gravities were found as follows:

$Cr_2Ba_3C_{12}O_{24}$	Anhydrous	2.570 at 6.8°
"	$6H_2O$.	2.445 at 13.9°
"	$12H_2O$.	2.372 at 27°

Here the second salt is nearly a mean between the other two.

The strontium salts were also prepared by Mr. Kebler, under varying conditions of temperature and dilution. These too came down as pale green satiny needles of considerable beauty, and easily recrystallizable from hot water. From cold dilute solutions the salt $Cr_2Sr_3C_{12}O_{24}.12H_2O$ was precipitated.

	Found.	Theory.
Cr	9.36	9.37
Sr	23.59	23.64
H_2O	19.29	19.45

From the mother liquor and washings of this salt a somewhat lower hydrate was deposited, possibly a mixture, corresponding in hydration to 10½ molecules of water. Specific gravity 2.148 at 8.8°. From hot concentrated solutions of the precipitants a decahydrated salt was obtained. Calling these salts A and B respectively, we have the following analytical data:

	Found.		Theory 10½ aq.	Theory 10 aq.
	A.	B.	A.	B.
Cr	9.55	9.52	9.59.	9.67
Sr	24.14	24.31	24.22	24.45
H_2O	17.36	16.87	17.40	16.75

I am inclined to look upon these preparations as mixtures of the twelve molecule salt with small quantities of a hexhydrated salt yet to be discovered.

The mother liquors from all these strontium precipitates were united and concentrated. Upon standing, a very dark green, almost black, crystalline crust was deposited. This, which had a specific gravity of 2.155 at 12.8°, proved to be a new triple oxalate having the formula $Cr_2Sr_2K_2C_{12}O_{24}$, with either eleven or twelve molecules of water.

	Found.	Theory, 11 aq.	Theory, 12 aq.
Cr	9.51	9.60	9.44
Sr	16.15	16.15	15.89
K	7.26	7.22	7.10
H_2O	18.33	18.28	19.61

I suspect that the twelve molecule formula is the true one, and that the salt as analyzed by Mr. Kebler may have been slightly effloresced. Still, the analytical agreement with the lower formula is wonderfully close.

The discovery of this new triple salt led to a search for the corresponding barium compound. The ordinary bario-chromic oxalate was accordingly dissolved with an equivalent quantity of the potassium salt in boiling water, and the mixture was then heated with barium carbonate in order to remove a little free oxalic acid which happened to be present as an impurity. Upon filtering, dull bluish green needles were deposited, having the composition $Cr_2Ba_2K_2C_{12}O_{24}$, with five or six molecules of water.

	Found.	Theory, 5 aq.	Theory, 6 aq.
Cr	9.86	9.68	9.53
Ba	24.25	25.51	25.09
K	7.41	7.28	7.14
H_2O	8.65	8.38	9.89

Since the salts which yield this triple salt each contained six molecules of water, I am inclined to consider that as the true degree of hydration for the compound now in question. In fact, throughout this series of complex oxalates, the hydration is almost uniformly six molecular, or represented by some even multiple of six. The chief exceptions are the lead and silver salts of Berlin, with 15 aq. and 9 aq. respectively; values which are regular submultiples of six.

The process by which these barium and strontium salts are prepared from the potassium salt is suggestive of their constitution. We may fairly regard the chromic oxalate itself as a weak acid, having the subjoined structural formula:

$$\left.\begin{matrix} H.C_2O_4 \\ H.C_2O_4 \\ H.C_2O_4 \end{matrix}\right\} Cr{-}Cr \left\{\begin{matrix} C_2O_4.H. \\ C_2O_4.H. \\ C_2O_4.H. \end{matrix}\right.$$

These six atoms of hydrogen are replaceable by six potassium atoms, by three barium atoms, or by two of each, and so on with

all the other salts of the series. If chromium be regarded as trivalent, the formulæ should of course be halved.

We attempted to prepare the sexbasic acid here suggested, but did not attain to final results. The barium salt was decomposed by an exactly equivalent quantity of sulphuric acid. Upon filtering, an acid liquid was obtained, strongly dichroic, and dark violet red by transmitted light. Probably this was the acid in question, but actual proof is yet wanting.

Mr. Kebler also tried to prepare several other salts of the series under discussion, but unsuccessfully. No calcium salt like that of Rees-Reece could be obtained. Calcium oxalate, slightly discolored by chromium, was thrown down every time. With salts of cadmium, cobalt, ferrous iron, zinc, copper, lead, and stannous tin, the blue potassio-chromic oxalate gives either no precipitate, or else, after some time, a precipitate of the ordinary oxalates of the metals in question. The filtrates from these oxalates afterwards deposit crystals, too impure for analysis, which appear to be the potassio-chromic salt of the red series. The plan of heating bario-chromic oxalate with the sulphates of cadmium, cobalt, copper, iron, and zinc was also tried. In each case an ordinary oxalate was formed, mixed with barium sulphate.

XXI.—THE TITRATION OF TARTARIC, MALIC AND CITRIC ACIDS WITH POTASSIUM PERMANGANATE—PRELIMINARY NOTE.

COMMUNICATED BY F. W. CLARKE.

Some time ago, in the course of certain investigations upon the tartrates of antimony, it occurred to me that tartaric acid, like oxalic acid, might perhaps be conveniently titrated with potassium permanganate. A single qualitative experiment showed that a fair end reaction was attainable, and the same thing proved to be true of malic and citric acids also. Accordingly I put the question into the hands of Mr. Miles Beamer, who made the following determinations:

The titrations were performed in all essential particulars exactly as for oxalic acid. A solution was prepared containing a definite

quantity of tartaric acid, and upon this the permanganate solution, which was approximately twentieth normal, was standardized. Sulphuric acid was of course added before titrating. The color changes were rather slower than with oxalic acid, and required a somewhat higher temperature. They were also possibly a trifle less delicate, but still fairly concordant results were easily obtained.

Having standardized the permanganate solution, it was used for estimating the percentage of tartaric acid in sodium potassium tartrate, $C_4H_4KNaO_6.4H_2O$. The following was the result, reckoning the acid as $C_4H_4O_6$:

Percentage found,	51.63
" theoretical,	52.48
Error,	0.85

As this percentage was rather roughly determined, a fresh experiment was made, with a new and more carefully standardized permanganate solution.

$C_4H_4O_6$ found,	52.75
Error,	0.27

Two sets of titrations were also made upon hydrogen potassium tartrate, $C_4H_5KO_6$. The percentages of acid, reckoned as $C_4H_5O_6$, came out as follows:

First set,	79.20
Second, "	78.88
Theory,	79.25

Tartar emetic was treated as follows: Its solution was mixed with a slight excess of ammonium sulphide, and then acidulated with dilute sulphuric acid. By warming and filtration, all the antimony was thus removed, and the tartaric acid was left in a suitable condition to be determined. The salt used, however, was found to have lost some of its crystalline water, so that the results were not comparable with theory. Other determinations are now in progress upon certain tartrates of antimony, and will be published in due time.

The experiments upon malic acid precisely resembled those upon tartaric acid, and were conducted by Mr. C. S. Evans. As we had no definite malates at hand, a standardized solution of malic acid was neutralized partly with caustic soda and partly with am-

monia. Thus solutions of alkaline malates were obtained containing known quantities of acid. Upon titrating these solutions, it was found that they behaved exactly like the acid itself. The ammonium malate gave 99.89 per cent. of the acid known to be present, while the sodium salt gave 100.007 per cent.

With citric acid the results are still very incomplete. Mr. L. R. Freeman standardized a solution of permanganate upon this acid, and found the final reaction to be fairly sharp, but very slow towards the end. This standard permanganate, applied to an analysis of trisodium citrate, gave in mean 53.36 per cent. of acid, reckoned as $C_6H_8O_7$. The theoretical amount should be 52.94. Error, 0.42. Mr. Evans attempted a repetition of these experiments, but, for some unknown reason, was not successful.

These preliminary figures show fairly well that the permanganate solution is suited to the titrations in question. The results may not be as sharp as with oxalic acid, but still they are fairly good. Some comparative titrations by Mr. Freeman show that tartaric and malic acids are oxidized to carbonic acid and water, while with citric acid the result is, of course, more complex. Although, then, it may be possible to standardize the permanganate upon oxalic acid once for all, I suspect it is better to standardize it directly upon whichever acid is actually to be estimated. I hope that either Mr. Beamer or myself will be able soon to present some additional figures.

XXII.—RELATION BETWEEN TEMPERATURE AND THE RATE OF CHEMICAL ACTION.

By R. B. Warder.

The speed of the reaction,

$$C_3H_5.O.C_2H_3O + NaOH = NaC_2H_3O_2 + C_3H_5OH,$$

in dilute aqueous solution, has been observed at temperatures from 3.6° to 37.7°C. This series of determinations nearly agrees with the equilateral hyperbola,

$$(7.5 + a)\,(62.5° - t) = 521.4,$$

where t is the temperature, and a expresses the number of gram-

equivalents per liter which would (according to the theory of the action of mass) react upon each other per minute in a solution kept of normal strength.

Further details are deferred to another number.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

IX.—OXIDATION OF SULPHAMINEMETATOLUIC ACID IN ALKALINE AND IN ACID SOLUTION.

By R. D. Coale and Ira Remsen.

In a paper entitled "Experiments in the Para-series,"[1] it has been shown that, when sulphamineparatoluic acid is oxidized with potassium permanganate in alkaline solution, it is transformed into the peculiar anhydride of sulphamineterephthalic acid called terephthalic sulphinide; whereas, when the oxidation is conducted in acid solution, the product is sulphoterephthalic acid. These results led to the examination of sulphaminemetatoluic acid—an examination which was particularly desirable, as a dispute had arisen in regard to the nature of the product formed when the acid mentioned is oxidized. One of us has repeatedly stated that the product formed when the free acid is treated with permanganate is sulphoisophthalic acid, while our opponent persistently denies this statement, and claims that the product is sulphamineisophthalic acid. In this paper it is shown that both of these acids, or at least the former and the anhydride of the latter, may be obtained at will, as readily as the corresponding para-compounds. To prove further that the substance obtained by oxidation in acid solution is in reality sulphoisophthalic acid, the latter has been prepared from xylenesulphonic acid directly, without the intermediate preparation of nitrogenous compounds. The results here recorded furnish a complete and final answer to the statements of our opponent above referred to, and they can

[1] This Journal, 2, 50.

leave no room for doubt regarding the accuracy of the statements already made by one of us in earlier papers of this series.

New Experiments on the Oxidation of Xylenesulphamides.

In the first paper of this series the oxidation of the amides of xylenesulphonic acids was fully discussed. As, however, in the course of the present investigation we have had occasion to oxidize large quantities of these amides, we have gained some new experience, the results of which are here briefly recorded. As regards the preparation of the amides, nothing need be added to the earlier statements. The separation was not carried to completion, and, indeed, without any separation a perfectly pure oxidation product may readily be obtained. At first, the partly purified amide was treated with the pyrochromate mixture, as directed in the first paper. In order to hasten the preparation of the acid, six hundred grams of the amide were divided into six equal portions, and each portion brought into a separate flask with the necessary quantity of the oxidizing mixture, no special precautions being taken in heating the flasks. The result of this was that scarcely a trace of the desired acid was obtained from each hundred grams of amide. The oxidation took place violently and the amide was almost completely destroyed. This brings to mind very vividly the first experiment performed in the oxidation of these amides, in which the same result led to the natural but erroneous conclusion that the amide which formed the principal bulk of the mixture used can not yield an acid by oxidation. In order to get the acid, it is necessary to go to work cautiously. Smaller quantities than those above mentioned should be taken, and, in heating, certain precautions must also be observed. As the result of a large number of experiments undertaken with the distinct object of determining the best conditions, we give the following specific directions for the oxidation of *a*-xylenesulphamide: The oxidizing mixture consists of 141 grams of potassium pyrochromate and 213 grams of ordinary concentrated sulphuric acid, diluted with three times its volume of water. After the mixture is cooled to the temperature of the air, 22 grams of the amide are added. The whole is then gently heated on the water-bath until the effervescence which indicates the beginning of the oxidizing action is seen. The flask is then connected with an inverted condenser, and the contents kept quietly

boiling for about an hour by means of a small free flame. The mixture is allowed to cool, and the oxidation product crystallizes out. The separation of this product from the little amide which remains unchanged is effected as described in the first paper already referred to. This unchanged amide is *remarkably pure α-amide*, which shows that the β-amide is completely destroyed, as has repeatedly been claimed. In the course of our work we obtained 85 grams of crude sulphaminemetatoluic acid, and this by recrystallization yielded 65 grams of finely crystallized pure acid. We examined the product with the greatest care with reference to the possible formation of an isomeric acid derived from the β-amide, but were unable to obtain the slightest evidence of the formation of such a substance. We may then unhesitatingly reaffirm the first statement that when a mixture of the α- and β-amides of xylenesulphonic acids is oxidized with chromic acid the β-amide is destroyed, while the α-amide yields a monobasic acid—sulphaminemetatoluic acid.

Oxidation in Acid Solution.

It has already been shown that when free sulphaminemetatoluic acid is treated with potassium permanganate, the product which is obtained in the form of the acid potassium salt is sulphoisophthalic acid. This salt is very easily obtained in perfectly pure condition, giving no evidence of the presence of nitrogen when tested according to Lassaigne's well-known method. In order to gain a more thorough knowledge of the tribasic sulphonic acid, a number of its salts were prepared and examined.

The starting point for the preparation of the salts was the acid potassium salt first obtained. As regards this salt, the only new fact to be recorded is that a determination of its solubility in water made according to the method devised by Victor Meyer, showed that 1.59 parts of the salt are soluble in 100 parts of water at 26°.

Neutral potassium sulphoisophthalate, $C_6H_3\begin{cases}SO_3K\\CO_2K.\\CO_2K\end{cases}$

This was obtained by exactly neutralizing a solution of the primary salt by means of a solution of potassium carbonate, and then evaporating to dryness. It is very easily soluble in water, and could not be made to crystallize. The results of the analysis, though

not satisfactory, show that the salt contains three atoms of potassium in the molecule.

0.2085 gram dried salt gave 0.1412 gram K_2SO_4.

Calculated.	Found.
32.56	30.40

An attempt was made to prepare the *secondary potassium salt*, $C_6H_3\begin{cases}SO_3K\\CO_2K\\CO_2H\end{cases}$, by dividing a solution of the primary salt into two equal parts, exactly neutralizing one-half with potassium carbonate and then bringing the two together. The solution was then evaporated, and a crystalline deposit obtained. This was found not to have a uniform composition. A similar result was reached by Remsen and Burney[1] in attempting to prepare the corresponding salt of sulphoterephthalic acid.

The *secondary barium salt*, $C_6H_3\begin{cases}SO_3\\CO_2\\CO_2H\end{cases}$ $Ba+xH_2O$, is the one originally obtained by Remsen and Iles.[2] We have found that the amount of water of crystallization which it contained varies, according to the conditions, from 1 to 2 molecules, and it appears from a single observation made on the same salt prepared in another way that it may contain even as much as 4 molecules. When the salt is prepared in the usual way by adding a solution of barium chloride to a boiling solution of the primary potassium salt, and then allowing the whole to cool, it contains 6.62 per cent. water, an amount which corresponds to 1½ molecules. This was clearly shown by a number of analyses made in the first part of the investigation, and the results have been confirmed by us. If, however, the solution of the primary potassium salt be rather dilute, and only *warm* when the barium chloride is added, then the barium salt takes a much longer time to crystallize out, and is obtained in larger crystals, which contain 8.63 per cent. of water. This indicates the presence of 2 molecules of water of crystallization. If the salt containing either 1½ or 2 molecules of water be kept in boiling water for a time, it loses its crystalline form to a great extent, and then contains but 4.51 per cent. of water, corresponding to 1 molecule.

The analyses here given show the variation in the amount of water of crystallization of the barium salt prepared at different temperatures.

[1] This Journal, **2**, 409. [2] Ibid. **1**, 126.

1. Salt prepared by adding barium chloride to a boiling solution of the primary potassium salt. 0.2067 gram salt lost 0.0137 gram H_2O at 212°.

Calculated for $1\frac{1}{2}H_2O$.	Found.
6.62	6.63

2. Salt prepared by adding barium chloride to a *warm, dilute solution* of the primary potassium salt. 0.2020 gram salt lost 0.0176 gram H_2O at 215°.

Calculated for $2H_2O$.	Found.
8.63	8.71

3. Salt after being in boiling water for a time. 0.2042 gram salt lost 0.0103 gram H_2O at 220°.

Calculated for $1H_2O$.	Found.
4.51	5.04

A determination of the solubility showed that only 0.071 part dissolves in 100 parts of water at 23.5°.

Primary barium salt, $\left(C_6H_3\begin{cases}SO_3\\CO_2H\\CO_2H\end{cases}\right)Ba$. The attempt to prepare this salt proved unsuccessful. The secondary salt dissolves readily in hydrochloric acid and probably the primary salt is in the solution, but we were unable to get it out in pure form, the composition of the product varying considerably.

Neutral barium sulphoisophthalate, $\left(C_6H_3\begin{cases}SO_3\\CO_2\\CO_2\end{cases}\right)_2Ba_3 + 3H_2O$.

This was prepared by boiling the secondary salt and barium carbonate together in water. On filtering and evaporating, a deposit was obtained which did not present a uniform appearance. The salt seemed to undergo some decomposition when its solution was evaporated. The character of the decomposition we have not, however, discovered. The deposit was analyzed with these results:

I. 0.2383 gram salt lost 0.0134 gram H_2O at 195° and gave 0.1711 gram $BaSO_4$.

II. 0.2069 gram salt gave 0.1484 gram $BaSO_4$.

	Calculated.	Found. I.	Found. II.
$3H_2O$ ...	5.68	5.62	...
Ba_3 ...	43.22	42.22	42.17

By boiling the secondary barium salt with sulphuric acid, filtering and evaporating to dryness, *free sulphoisophthalic acid* was obtained. It is very easily soluble in water and hygroscopic. After standing for several days over sulphuric acid it was obtained as a semi-crystalline mass fusing at 243-244° (uncorr.). In the paper already referred to the fusing point of the acid is stated to be 285–287°. This must be an error. It is possible that in some of the earlier preparations the sulphamineisophthalic acid may have been obtained, and that this may have been the substance used in making the original determinations, as at that time it was not known that both the non nitrogenous and the nitrogenous acids may be obtained by oxidation of sulphaminemetatoluic acid.

The existence of the salts above described, notwithstanding their unattractive properties, serves to show, at least, that the acid from which they are derived is tribasic; and when the descriptions of these salts are compared with those of the salts of sulphamineisophthalic acid, as will be done below, it will be seen that there is no possibility of confounding the two series of compounds.

Oxidation in Alkaline Solution.

Remsen and Hall[1] have shown that the addition of an alkali to the oxidizing mixture in the case of sulphaminemetatoluic acid causes the formation of terephthalic sulphinide. We have obtained a similar result with the meta acid.[2] The acid was treated with the oxidizing mixture in these proportions: 5 grams acid, 20 grams potassium permanganate, water 190 cc., and 10 cc. caustic potassa containing 2.3 grams potassium hydroxide, or an excess of one gram above the amount required for the neutralization of the acid.

The mixture was heated for five or six hours on the water-bath; the reduction completed by means of a few drops of alcohol; the solution filtered and evaporated to a small volume. Hydrochloric acid was now added, and on cooling the product crystallized out. One recrystallization is usually sufficient to purify it. The substance thus obtained crystallizes well, and fuses at 282.5° (uncorr.). Lassaigne's test shows the presence of nitrogen without difficulty. The analyses proved that the substance is anhydrosulphamineisophthalic acid or *isophthalic sulphinide*.

[1] This Journal, **2**, 132. [2] Berichte der deutsch. chem. Gesell. **12**, 1436.

Calculated for $C_6H_3\begin{cases}SO_2\\CONH.\\CO_2H\end{cases}$		Found.	
		I.	II.
S ...	14.09	14.41	14.34
N ...	6.14	6.50	6.34

Mono-potassium anhydrosulphamineisophthalate, $C_6H_3\begin{cases}SO_2\\CONH+\\CO_2K\end{cases}2H_2O$. This salt was prepared by adding the required amount of potassium carbonate in solution to a solution of the sulphinide. The solution was then evaporated to a small volume, and, on cooling, the salt crystallized out. It crystallizes in well formed, transparent, rectangular prisms, which lose their water of crystallization at 110–120°. The analyses gave these results:

Calculated for $C_6H_3\begin{cases}SO_2\\CONH+2H_2O.\\CO_2K\end{cases}$		Found.	
		I.	II.
K ...	12.99	12.93	12.96
$2H_2O$ ...	11.92	11.89	11.80

To establish the bibasicity of the acid, neutralization experiments were made with the results here stated. Two portions of the acid potassium salt were treated with a standard solution of ammonia. On the assumption that the acid is bibasic, the quantities of the standard ammonia solution calculated as compared with the quantities used are as follows:

	Calculated.	Used.
I.	5.8 cc.	5.76 cc.
II.	5.5 cc.	5.54 cc.

2.3 parts of the salt are soluble in 100 parts of water at 26.3°.

Neutral potassium sulphamineisophthalate, $C_6H_3\begin{cases}SO_2NH_2\\CO_2K\\CO_2K\end{cases}+4H_2O$. This was prepared by exactly neutralizing the acid potassium salt. On evaporating almost to dryness and cooling, the salt crystallized in long needles, but owing to its extreme solubility it could not be obtained dry in good crystals. Analyses were made with these results.

I. 0.204 gram salt lost 0.0381 gram H_2O at 120°, and gave 0.0938 gram K_2SO_4.

II. 0.2100 gram salt lost 0.0377 gram H_2O at 130°, and gave 0.0986 gram K_2SO_4.

Calculated for $C_6H_3\{SO_2NH_2, CO_2K, CO_2K + 4H_2O$.		Found.	
		I.	II.
K_2	19.88	20.64	21.07
$4H_2O$	18.31	18.68	17.95

Acid calcium anhydrosulphamineisophthalate, $\left(C_6H_3\{SO_2{-}, CONH, CO_2\}_2\right)Ca + xH_2O$. This was prepared by dividing a solution of the free acid into two parts, neutralizing one-half and then bringing the two together. On evaporating to a small volume, the salt separated partly in amorphous form and partly in feather-shaped crystalline masses. It loses water rapidly, so that no accurate determination of the entire amount of water of crystallization first contained in the salt can be made. Dried in the air it contains 4 molecules, which are given off at 150°. The analyses here recorded prove the composition of the salt.

I. 0.2143 gram salt lost 0.0263 gram H_2O at 150°, and gave 0.0522 gram $CaSO_4$.

II. 0.2276 gram salt lost 0.0286 gram H_2O at 150°, and gave 0.0553 gram $CaSO_4$.

	Calculated.	Found.	
		I.	II.
Ca	7.09	7.16	7.15
$4H_2O$	12.77	12.27	12.57

Calcium sulphamineisophthalate, $C_6H_3\{SO_2NH_2, CO_2, CO_2\}Ca + 6H_2O$, was obtained by boiling a solution of the acid with finely powdered Iceland spar. On evaporating to a small volume it crystallizes out in large, finely developed apparently monoclinic crystals. These crystals rapidly lose three molecules of their water of crystallization on exposure to the air, and this loss is accompanied by a complete transformation of the crystals. They become opaque and fall to pieces, forming an amorphous powder. This powder, however, still contains 3 molecules of water which are not given off below 170–180°.

The crystals first obtained gave these results:

0.4214 gram salt lost 0.1181 gram H_2O at 180°, and gave 0.1531 gram $CaSO_4$.

	Calculated.	Found.
Ca	10.23	10.68
$6H_2O$	27.62	28.03

The results obtained in the analysis of the air-dried salt are as follows:

0.2004 gram salt lost 0.0341 gram H_2O at 190°, and gave 0.0806 gram $CaSO_4$.

	Calculated.	Found.
Ca	11.87	11.83
$3H_2O$	16.02	17.02

Acid barium anhydrosulphamineisophthalate, $\left(C_6H_3\left\{\begin{matrix}SO_2\\CONH\\CO_2\end{matrix}\right\}\right)_2Ba+4H_2O$. To obtain this salt the most convenient method is to boil a solution of the acid potassium salt with barium chloride. This is also the method best adapted to the preparation of the acid barium salt of sulphoisophthalic acid. In the latter case, however, a precipitate is produced almost instantly, and very violent "bumping" is produced; while in the former case no precipitate is formed, and the clear liquid boils quietly. On cooling, if the solution be sufficiently concentrated, the acid barium salt crystallizes out in well formed, transparent, monoclinic plates, which lose their water of crystallization at 100–105°. The analysis gave the accompanying results:

0.1777 gram salt lost 0.0201 gram H_2O at 110°, and gave 0.0625 gram $BaSO_4$.

	Calculated.	Found.
Ba	20.68	20.72
$4H_2O$	10.89	11.31

Barium sulphamineisophthalate, $C_6H_3\left\{\begin{matrix}SO_2NH_2\\CO_2\\CO_2\end{matrix}\right\}Ba+4H_2O$, was prepared by boiling the acid with barium carbonate in a large volume of water, as the salt is difficultly soluble. It is obtained in large, well formed, thick monoclinic plates, which lose part of their water of crystallization when exposed to the air, become opaque and fall to pieces. If a solution of the salt be boiled, a

white powder is deposited, a partial decomposition apparently taking place. In the crystallized form the salt contains 4 molecules of water of crystallization. A rapid determination gave 16.28 per cent. water, while 15.93 per cent. are required for $4H_2O$. The air-dried salt contains varying amounts of water, and analyses were therefore made of the salt dried at 130°.

0.2215 gram salt gave 0.1365 gram $BaSO_4$.

	Calculated.	Found.
Ba	36.21	36.23.

From the descriptions of the salts derived from sulphoisophthalic acid and from sulphamineisophthalic acid, it will be seen that there is very little resemblance between the corresponding members of the two series. In general, the salts of the latter acid are more easily prepared, and have better properties than those of the sulphonic acid. The difficulties met with in the preparation of the neutral salts of the tribasic sulphonic acid suggest the experiences in connection with sulphoterephthalic acid already recorded, but the results obtained with both these acids leave no room for doubt that they are really *tribasic*. Since the publication of the paper on sulphoterephthalic acid, P. Schoop[1] has stated that owing to the impossibility of obtaining neutral salts of sulphoterephthalic acid, prepared by treating terephthalic acid with "solid sulphuric acid," the sulphonic acid must be regarded as *bibasic*. This conclusion certainly does not apply to the sulphonic acid previously described, and it is difficult to see how two sulphoterephthalic acids can be formed, though, of course, two *may* be possible.

As a result of the experiments treated of in this paper, it will be seen that when sulphaminemetatoluic acid, $C_6H_3\begin{cases}SO_2NH_2\\CH_3\\CO_2H\end{cases}$ is oxidized in acid solution, *i. e.* when the free acid is oxidized, without the addition of an alkali, with potassium permanganate, the product is *sulphoisophthalic acid*, $C_6H_3\begin{cases}SO_3OH\\CO_2H.\\CO_2H\end{cases}$ Whereas, if a quantity of alkali but slightly in excess of that required to neutralize the acid be added, and the oxidation be carried on otherwise in exactly the same way as in the first experiment, the product is *isophthalic sulphinide*, $C_6H_3\begin{cases}SO_2\\CO\ NH\\CO_2H.\end{cases}$

[1] Berichte d. deutsch. chem. Gesell. **14**, 223.

Sulphoisophthalic Acid from Metaxylenesulphonic Acid.

To make the proof concerning the nature of the substance called sulphoisophthalic acid complete, metaxylenesulphonic acid itself was oxidized, and the tribasic acid thus formed compared with that obtained by oxidizing sulphaminemetatoluic acid.

The potassium salts of the crude mixture of xylenesulphonic acids obtained by direct treatment of purified commercial xylene with sulphuric acid were subjected to oxidation in two stages, potassium pyrochromate being first used and then permanganate, as was done in the experiments with paraxylene and cymene. Though no special experiments have been performed with reference to this point, it appears from the observations here made that the permanganate acts most readily on the oxidizable groups situated in the ortho-position; so that, if an ortho- and a para-group, or an ortho- and a meta-group be present together in the compound, the action first takes place in the ortho-group, and there seems to be considerable difficulty in effecting the oxidation of the other groups without complete decomposition of the compound. At all events, we have always obtained much more satisfactory results by oxidizing first with chromic acid, the action of which goes no farther than the para- and meta-groups, the ortho-group being unacted upon; and then effecting the oxidation of the latter with permanganate. The yield was in no case satisfactory, but still we obtained enough of the product to enable us to make the desired comparison. The details of the process were the same as those described in the paper by Remsen and Kuhara,[1] and they need not here be repeated. An acid potassium salt was obtained, which in every respect resembles the acid potassium salt obtained by oxidation of sulphaminemetatoluic acid in acid solution. The analysis shows that the salt also has the same composition, $C_6H_3\begin{cases}SO_3K\\CO_2H\\CO_2H\end{cases} + 2H_2O$.

0.2059 gram salt lost 0.0230 gram H_2O at 140° and gave 0.0568 gram K_2SO_4.

	Calculated.	Found.
K	12.21	12.38
$2H_2O$	11.25	11.17

[1] This Journal, **2**, 413.

On boiling a solution of this salt with barium chloride, all the characteristic phenomena observed in connection with the acid potassium salt first described were repeated. The precipitate was readily formed, and at once the most violent "bumping" began. The barium salt thus obtained proved to be secondary barium sulphoisophthalate, as was expected. Variations in the amount of water of crystallization contained in the salt prepared under different conditions were observed in this case as well as in that described in the earlier part of this paper. Indeed, in one preparation as much as 4 molecules of water were found, but, though attempts were made to obtain this salt a second time, they were unsuccessful. The properties of the salt were in every respect identical with those of the same salt prepared from the sulphamine acid.

A solubility determination showed that 0.075 parts dissolve in 100 parts of water at 23.5°. A similar determination with the salt first obtained showed that 0.071 parts dissolve in 100 parts water.

The analyses gave these results:

1. Salt prepared by adding barium chloride to a cold solution of the acid potassium salt.

I. 0.2042 gram salt lost 0.0306 gram H_2O at 218° and gave 0.1055 gram $BaSO_4$.

II. 0.2011 gram salt lost 0.0299 gram H_2O at 218° and gave 0.1043 gram $BaSO_4$.

Calculated for $C_6H_3\begin{cases}SO_3\\CO_2\\CO_2H\end{cases}Ba+4H_2O$.		Found.	
		I.	II.
Ba	30.24	30.38	30.50
$4H_2O$	15.85	14.99	14.87

2. Salt prepared from a warm solution:

0.2008 gram salt lost 0.0172 gram H_2O at 225°.

Calculated for $2H_2O$.	Found.
8.63	8.57

3. Salt boiled under water:

0.2042 gram salt lost 0.0103 gram H_2O at 220°.

Calculated for $1H_2O$.	Found.
4.51	5.04

The acid here described as obtained by the oxidation of metaxylenesulphonic acid has also recently been described elsewhere.

This description[1] agrees in the main with ours. The only difference observed is in the amount of water of crystallization in the acid barium salt. In the paper referred to it is stated that the salt contains three molecules of water. We have never analyzed a specimen containing this amount, but as the amount present is, to some extent, a matter of accident, it is very possible that under some circumstances a salt containing three molecules may be met with.

There can then be no doubt that the substance formed when sulphaminemetatoluic acid is oxidized in acid solution is in reality sulphoisophthalic acid, as has constantly been claimed by one of us. With this communication we may certainly regard the discussion in regard to the nature of the substance, as definitely concluded.

X.—CONCERNING MESITYLENIC SULPHINIDE.

By Ira Remsen and P. H. Broun.

At the conclusion of a paper on "Experiments with Mesitylene,"[2] an account of some unfinished experiments was given, which were undertaken with the object of determining the nature of the product formed by treating mesitylenesulphamide with chromic acid. These experiments have been continued by us and have led to the desired object. It will be remembered that when mesitylenesulphamide is treated with the ordinary chromic acid oxidizing mixture, only one of the three methyl groups contained in the compound is converted into carboxyl. It was at first believed that this result could be explained by the assumption that the substituting group exerts a protective influence on two of the methyl groups, with reference to which it occupies the ortho-position, while not interfering with the oxidation of the one methyl in the para-position. This conclusion was supported by analogy; and since the subject was first taken up in this laboratory, a number of cases have been added to those upon which the general idea of protection from oxidation is based. It is coming to be generally recognized that the law first enunciated in these papers, and which lies at the bottom of the transformations discussed in them, is valid; and if the

[1] Berichte d. deutsch. chem. Gesell. **13**, 1556. [2] This Journal, **2**, 130.

fact were made known to-day, for the first time, that the oxidation product obtained from mesitylenesulphamide is a monobasic acid, most chemists would, we think, consider it very probable that the product has the formula first provisionally assigned to it, according to which the sulphamine group is in the ortho-position with reference to the two methyl groups. This would appear all the more probable from the fact that when nitromesitylene and brommesitylene are oxidized, the nitro-group and the bromine atom actually protect the two ortho-methyls, as has been proved by Schmitz.[1] At the conclusion of his paper Schmitz says: "Das Brom und die Nitrogruppe üben also einen schützenden Einfluss auf die benachbarten beiden Methylatome aus."

We regret to say, however, that the conclusion which appears so probable has proved to be incorrect. In the first paper on this subject it was shown by a number of analyses that the product of oxidation under discussion is in reality one of the class of sulphinides; it is sulphaminemesitylenic acid less the elements of water. This suggested at once that possibly our first conclusion was wrong. Jacobsen's experiments,[2] which were taken up in the mean time, also indicated clearly that our first formula was not in accordance with all the facts.

To still further test the matter, which is one of considerable importance, we have started from mesitylenic acid and from this made the sulphonic acids. These were separated, and one of them converted, on the one hand, into ordinary oxymesitylenic acid, and, on the other, into mesitylenic sulphinide; thus proving that the sulphinide or the oxidation product in question has a structure analogous to that of ordinary oxymesitylenic acid. As Jacobsen had previously shown that his parasulphaminemesitylenic acid corresponds to a new oxymesitylenic acid, which is called paraoxymesitylenic acid, the proofs in regard to the nature of the sulphinide are complete.

Sulphomesitylenic Acids.

In preparing mesitylenic acid we followed at first the directions originally given, using nitric acid of sp. gr. 1.4, diluted with twice its volume of water. It was soon found, however, that the yield was very small, large quantities of nitromesitylenic acid being formed. According to our experiments a much larger yield is

[1] Annalen der Chemie, **193**, 160. [2] Ibid. **206**, 167.

obtained by using more dilute nitric acid, and we recommend the use of acid of sp. gr. 1.35, diluted with twice its volume of water. The mesitylenic acid was purified in the usual manner, and, when dry, subjected to the influence of the fumes of sulphuric anhydride for about forty-eight hours. At the end of this time the greater part of the acid had passed into solution, forming a dark viscous liquid. It was largely diluted with water and filtered from some unchanged acid, and was then of a beautiful red color. Neutralization was effected with chalk, and the filtered solution of the calcium salts decolorized with animal charcoal. The salts are easily soluble in water, and cannot be readily separated from each other. By repeated recrystallizations two salts were obtained in well-formed crystals, differing somewhat from each other, though by no means markedly. The less soluble salt is designated as the α-salt, and the other as the β-salt. Both were analyzed. The α-salt gave the following results:

I. 0.2011 gram salt lost 0.0411 gram H_2O, and gave 0.08378 gram $CaSO_4$.

II. 0.1757 gram salt lost 0.0358 gram H_2O, and gave 0.0735 gram $CaSO_4$.

Calculated for $C_6H_2\{^{SO_3}_{CO_2}\}\{^{Ca}_{CH_3}\}_2 + 4H_2O$.		Found. I.	II.
Ca	14.93	15.40	15.45
$4H_2O$	21.18	20.44	20.38

The results with the β-salt were almost exactly the same as those just given.

I. 0.2586 gram lost 0.0529 gram H_2O and gave 0.1043 gram $CaSO_4$.

II. 0.2071 gram lost 0.042 gram H_2O and gave .0835 gram $CaSO_4$.

Calculated.		Found. I.	II.
Ca	14.93	14.87	14.91
$4H_2O$	21.18	20.28	20.45

The deficit in the water is probably to be referred to efflorescence, as the crystals lose their lustre to some extent on exposure to the air.

Whether we have actually to deal with two salts is perhaps a question, but it is not a question of much importance, as far as the use to which the salts are put in this investigation is concerned.

The main point to be attended to, a point of vital importance for our purpose, was to secure at least one salt of a sulphomesitylenic acid in unquestionably pure condition, and this we have done.

We attempted a separation of the two acids by preparing the barium salts, but our attempts were not attended with much success. One of the barium salts is exceedingly difficultly soluble. This was repeatedly boiled with water to extract any soluble salt that might be present, and then remained in the form of a heavy amorphous powder which, on analysis, was found to contain 37.3 per cent. barium, the calculated amount being 37.53 per cent. The soluble barium salt was not obtained in anything like pure condition and was not further examined.

Transformation of α-Sulphomesitylenic Acid into the Sulphinide.

The α-calcium salt above referred to was converted into the corresponding potassium salt and the solution evaporated to dryness. One-half of this potassium salt of α-sulphomesitylenic acid was treated with phosphorus pentachloride and ammonia. Most of the chloride formed in the first reaction dissolves in ammonia. On filtering from a small quantity of material, the nature of which was not determined, and adding hydrochloric acid, a copious precipitate was obtained. This proved to be nothing but mesitylenic sulphinide. Its appearance, fusing point, solubility and general conduct could not leave a doubt in regard to the identity of the two substances. The reaction suggests one described some time since by Remsen and Fahlberg[1] in connection with orthosulphobenzoic acid. This acid when treated with phosphorus pentachloride and ammonia is converted into benzoic sulphinide. Other similar cases have since been observed in this laboratory. In all of them the common feature of the compounds concerned is the ortho-position of the sulpho-group and carboxyl, so that it appears probable that in α-sulphomesitylenic acid also these two groups are in the ortho-position with reference to each other, and consequently that, in the sulphinide, a similar relation exists between the residues of sulphamide and carboxyl.

The formation of mesitylenic sulphinide by the reaction above described appears strange when we remember that the sulphinide itself when treated with the same reagents is converted into a new product fusing at 287°, probably a double amide.[2] On taking

[1] This Journal, **1**, 426. [2] This Journal, **2**, 143.

some of the sulphinide prepared by us, converting it into the potassium salt and treating it with phosphorus pentachloride and ammonia, a new substance was obtained identical with that obtained from the original sulphinide. The two substances were carefully compared with each other and no difference observed. Both fused at 288° according to our thermometer; both are very difficultly soluble in water, and both crystallize in very delicate needles. This supposed double amide is not decomposed by hydrochloric acid even when the latter is concentrated and boiling, so that it is plain that this is not the product first obtained from *a*-sulphomesitylenic acid, as might be supposed. The facts are probably these: When potassium sulphomesitylenate is treated with phosphorus pentachloride, only one of the acid hydroxyl groups is replaced by chlorine. On now treating this chloride with ammonia, the ammonium salt of sulphaminemesitylenic acid is formed, and the addition of hydrochloric acid precipitates the sulphinide. It is possible that the substance above referred to as insoluble in ammonia may have been the double chloride of sulphomesitylenic acid, and that this resists the action of ammonia. When the potassium salt prepared from the sulphinide is treated with phosphorus pentachloride, the chloride is easily formed, and this is readily acted upon by ammonia and converted into the diamide. As yet these statements lack proof.

Transformation of a-Sulphomesitylenic Acid into Ortho-oxymesitylenic Acid.

The second half of the potassium salt used in the last experiment was fused with potassium hydroxide, and the corresponding oxyacid was readily obtained. The latter was precipitated on acidifying the alkaline aqueous solution of the fused mass. It was filtered off and washed and then brought into a flask with water and boiled. It passed over readily with the water vapor, and was thus easily obtained in pure condition. All the properties of the substance are those of ordinary oxymesitylenic acid. It fuses at 176°, and its solution is colored blue by ferric chloride. It is difficultly soluble in water. These properties, when taken together with its volatility with water vapor, prove that it is identical with ortho-oxymesitylenic acid. No trace of para-oxymesitylenic acid could be detected, though ether extracted a small quantity of a second

acid from the original mother liquor from oxymesitylenic acid. This was certainly not para-oxymesitylenic acid, but rather, in all probability, an oxyuvitic acid. Its quantity was too small to permit of its thorough examination.

Thus it will be seen that, while mesitylenic sulphinide, when fused with potassium hydroxide, is converted into mesitylenic acid, the corresponding sulphonic acid acts as such acids usually do, yielding the oxy-acid.

The most important result of this investigation is the conversion of a pure potassium salt of sulphomesitylenic acid into mesitylenic sulphinide on the one hand, and into ortho-oxymesitylenic on the other. The proofs of the structure of mesitylenic sulphinide are thus complete.

REVIEWS AND REPORTS.

Report on Progress in Physiological Chemistry.

Salivary Digestion and the Products formed.

In 1831 Leuchs made the interesting discovery that saliva, the first digestive fluid with which food comes in contact, possessed the property of converting insoluble starch into soluble dextrin and sugar. Later it was found that saliva exercised this property only slowly and with difficulty upon raw starch, while roasted starch and starch paste, in which the individual starch grains were ruptured, were rapidly converted into soluble saccharine products. This important property of saliva was soon ascribed to the presence of a peculiar diastatic ferment, which received the name of ptyalin, a small quantity of which was supposed to possess the property of converting an indefinite amount of starch into sugar without being itself used up or destroyed. According to Paschutin's[1] observations, however, the ferment of saliva can convert only a limited quantity of starch into dextrin and sugar, for saliva which has once served this purpose, on being used a second time works with much less activity than when fresh, and this appears to be independent of any hindering action due to the presence of the products of digestion.

The old and generally adopted view in regard to the decomposition of starch by salivary and similar ferments as well as by dilute sulphuric acid, was that the starch was first converted into isomeric

[1] Centralbl. f. d. med. Wiss. 1871, 24.

dextrin, and then further changed by taking up a molecule of water into dextrose. In 1860, however, Musculus,[1] while studying the action of diastase on starch, was led to the belief that the formation of sugar was the result of a splitting up of the starch molecule according to the following equation:

$$3C_6H_{10}O_5+2H_2O=C_6H_{12}O_6+2C_6H_{10}O_5,$$

inasmuch as he found that a mixture of diastase and starch heated at 70°C gave a fluid in which dextrose and dextrin were always present in the proportion of 1 : 2. Later, Payen,[2] and still later, Schulze and Märker,[3] have shown conclusively that diastase converts only a limited quantity of the starch into dextrose, and that no matter how great the excess of ferment or the length of time the action is continued, the quantity of sugar formed never exceeds 53 per cent. This amount of sugar agrees very closely with the quantity required on the supposition that two molecules of starch break up into equal molecules of dextrin and dextrose according to the following formula:

$$2C_6H_{10}O_5+H_2O=C_6H_{10}O_5+C_6H_{12}O_6.$$

That a dextrin is formed under these circumstances, which withstands the further action of diastase, has been recently and clearly shown by Musculus and Gruber,[4] who subjected starch paste to the action of diastase for five consecutive days, and then separated the remaining dextrin by precipitation with alcohol. The dextrin thus formed, on being tested, was found to be wholly unaffected by the further action of diastase. The exact expression of this decomposition is naturally dependent, in part at least, on the composition of the starch molecule, a fact which is not yet wholly settled. That the starch molecule is much larger than hitherto supposed is more than probable, and the researches of Bondonneau, Sachsse, and particularly Nägeli,[5] would seem to indicate that its composition is more correctly expressed by the formula $C_{36}H_{62}O_{31}$, which is exactly six times $C_6H_{10}O_5$+one molecule of water.

The next knowledge gained in regard to the decomposition of starch by ferments tended to complicate the question still further, for it was found that instead of there being only one dextrin, there were at least two, possessed of widely different qualities. At the same time Brücke[6] found that starch grains contain three distinct substances, granulose colored blue by iodine, erythrogranulose colored red, and cellulose, which either remains unchanged or is colored slightly yellow by iodine. Thus, when a small quantity of starch is mixed with a few drops of a strong iodine solution, the starch grains are colored deep blue, owing to the excessive amount of granulose, but if a small quantity of a dilute iodine solution is added to starch suspended in water and the mixture thoroughly shaken to ensure equable distribution of the iodine

[1] Chem. Centralbl. 1860, 603.
[2] Chem. Centralbl. 1865, 845.
[3] Chem. Centralbl. 1872, 823.
[4] Zeitschrift für Physiolog. Chem. 2, 177.
[5] Beiträge zur Kenntniss der Stärkegruppe, 34.
[6] Sitzungsber. d. Wiener Acad. III Abtheil. 1872.

among all of the starch grains, a pale red color is obtained. This reaction is due to the fact that the erythrogranulose, which is present in relatively smaller quantity in starch, has a stronger affinity for iodine than the granulose has, and consequently when but a small quantity of iodine is present the erythrogranulose combines with it exclusively, leaving the granulose and cellulose uncolored. Now, when starch is boiled with very dilute sulphuric acid, it is converted first into soluble starch or the amidulin of Nasse, and then into dextrin and sugar,[1] but in investigating the different stages of this change Brücke found two distinct kinds of dextrin. Thus, by the first action of boiling dilute sulphuric acid or of diastase, the granulose and then the erythrogranulose, are converted into a dextrin colored red by iodine, called erythrodextrin. By the further action of the dilute acid or of diastase this dextrin is changed into achroodextrin, which is not colored by iodine, and sugar. The achroodextrin by the combined action of acids or of ferments remains unchanged, or is but slowly decomposed, and this fact according to Brücke constitutes the main grounds of distinction between erythro- and achroodextrin.

That a certain quantity of saliva will act only on a certain quantity of starch is likewise made clear by the fact that the products of this transformation are variable, depending on the quantity of saliva employed; thus it has been found by experiment[2] that when a proportionately large quantity of saliva and a relatively small quantity of starch paste are employed, scarcely any erythrodextrin is found, this product being almost immediately further converted into achroodextrin and sugar. When on the other hand a very small quantity of saliva and a large quantity of starch paste are taken, considerable quantities of erythrodextrin are found. Thus these facts tend to corroborate Paschutin's observations that the ferment of saliva can convert only a limited quantity of starch into sugar, while at the same time it would appear that the first action of saliva consists in converting the granulose and erythrogranulose of starch into erythrodextrin, and this is followed, when sufficient ferment is present, by the further conversion of erythrodextrin into achroodextrin and sugar.

The ptyalin of saliva does not appear to differ from the diastatic ferment of the pancreas and other glands, and is likewise very similar in its action to extract of malt, excepting in the temperature at which the conversion of starch takes place. On the authority of Paschutin and Kühne, human saliva diluted ten times converts starch into dextrin and sugar most rapidly at 35–41° C, while the strongest action of malt ferment is at 70° C. In 1877 O. Nasse[3] attempted to show that the sugar formed from starch, glycogen, and likewise from Brücke's achroodextrin, by the action of saliva was not dextrose, but a saccharine body possessed of peculiar

[1] Discovered by C. Kirchhoff in 1811. [2] Brücke loc. cit.
[3] Pflügers Archiv. f. p. ges. Physiol. **14**, 473.

properties. This substance, which Nasse called ptyalose, possessed only half as great a reducing power as dextrose, was less soluble in alcohol, and was converted into dextrose by boiling with dilute sulphuric acid. In 1878 V. Mering and Musculus[1] called attention to the old statement of Dubrunfant, made in 1847, that by the action of malt on amylum a sugar was formed which was not dextrose, and which he termed maltose. This statement was for some time doubted, but recently the above investigators, calling attention to the works of O. Sullivan and E. Schultze,[2] have attempted to confirm this view. Maltose, $C_{12}H_{22}O_{11}+H_2O$, differs from dextrose by possessing a rotatory power three times greater and one-third as great a reducing power. By boiling with dilute acids, maltose is changed into dextrose, and it may thus be considered as a body intermediate between dextrin and dextrose. Now, the fact that starch, under the influence of diastase, is converted into maltose, and not into dextrose, has led Musculus and Mering to the supposition that starch, and likewise glycogen, under the influence of other ferments, as saliva and pancreas, may be converted into maltose, although not, perhaps, as an end product. They find, as a result of careful investigation,[3] that the action of saliva on starch is completely analogous to the action of diastase, viz. achroodextrin and maltose are formed, together with a small quantity of dextrose, the latter being present to the extent of 1 per cent, while the quantity of maltose is about 70 per cent. Nasse's[4] view that a new saccharine body ptyalose is formed is shown by Musculus and Mering to be incorrect. At the same time Nasse's statement that his ptyalose has its reducing power increased twofold by boiling with acids prepares us for the statement of Musculus that the so-called ptyalose is a mixture of maltose, dextrin and possibly a little dextrose. Glycogen prepared from liver treated with saliva for ten hours at 15°C yielded Musculus and Mering an achroodextrin which possessed the property of reducing alkaline copper solutions, maltose and small quantities of dextrose. The same result was obtained by the action of diastase. The same products were also formed by the action of pancreatic ferment on starch, in every case maltose being the predominant product.

Musculus, in conjunction with Gruber,[5] has likewise found that starch, by the action of diastase or acids, in splitting up with formation of maltose, soluble starch, dextrose and dextrin, gives rise to different kinds of achroodextrin, which are distinguished one from the other by the ease or difficulty with which they are attacked by ferments, as well as by certain differences in their chemical properties.

[1] Zeitschrift für Physiolog. Chem. **1**, 395.
[2] Bericht. d. deutsch. chem. Gesell. **7**, 1047. Schultze found that, by the action of vegetable diastase on amylum, achroodextrin and maltose were formed, the latter of which differed essentially from Nasse's ptyalose.
[3] Zeitschrift für Physiolog. Chem. **2**, 403.
[4] Pflügers Archiv. **14**.
[5] Zeitschrift für Physiolog. Chem. **3**, 177.

Thus the following table represents, according to these investigators, the different products formed from starch by diastase:

	Rotatory Power.	Relative Power of Reduction.	Iodine Reaction.
Soluble Starch,	218°	6	red (blue.)
Erythrodextrin,	...	...	red.
α Achroodextrin,	210°	12	colorless.
β "	190°	12	"
γ "	150°	28	"
Maltose,	150°	66	"
Dextrose,	56°	100	"

Recently Dr. E. H. Bimmerman,[1] of Amsterdam, has confirmed the results of Musculus and Mering; for, by digesting 100 grams of potato starch with 1 litre of water and 800 cc. of filtered mixed saliva for five hours at 30–40°C, he obtained crystallized maltose, a dextrin possessing reducing properties, and a small quantity of dextrose. Bimmerman has likewise studied the changes which these products of salivary digestion undergo in the blood, and, as a result of his work, finds that when maltose is injected into the blood of a rabbit, for example, the urine contains maltose and dextrose, thus showing that maltose in the blood is partly changed into dextrose and partly excreted by the organism undecomposed. Soluble starch or amidulin injected into the blood in a similar manner was found to be wholly changed into dextrin and dextrose, both of which were detected in the urine. Achroodextrin α under the same circumstances was found to be only partially decomposed, the decomposition products being dextrose and maltose.

Carrying the experiments still farther, Bimmerman[2] finally arrives at the conclusion that starch in the blood undergoes changes in the same manner as by animal and vegetable diastatic ferments outside the body. Thus, for example, soluble starch and dextrin α readily yield under the influence of changes taking place in the blood readily-fermentable sugar, dextrin β difficultly fermentable sugar, and dextrin γ none at all, which is in accord with the action of ferments outside of the body. Maltose, on the other hand, which is not attacked by ferments, undergoes, in contact with the circulating blood, a slight, but still appreciable, change into dextrose, while dextrin γ in the circulating blood yields no sugar, but is apparently converted into another form of dextrin, which possesses a higher reducing power, and to which the name dextrin δ has been given; a compound which also appears to be formed whenever amylum or starch is attacked very energetically by ferments or dilute acids. Seegen,[3] of Vienna, has also studied the action of salivary and pancreatic ferments on glycogen and other forms of amylaceous matter, and, he, too, has come to the conclusion independently of Musculus that the sugar formed from both glycogen

[1] Pflügers Archiv. **20,** 291. [2] Loc. cit. 209–210. [3] Pflügers Archiv. **19,** 122.

and starch by the action of saliva, pancreas, and diastase is not dextrose, but a sugar possessed of less reducing power and a higher specific rotatory power. Thus, by the action of saliva on glycogen, a sugar was formed having a specific rotatory power of 119°, which is more than twice as great as that of dextrose, and a reducing power amounting to 68 per cent., which is about one-third smaller than that of dextrose.

According to his observations also glycogen is, under the influence of ferments, quickly converted into achroodextrin. This change is finished when the original opalescence of the glycogen solution is changed to a clear and transparent one, but the achroodextrin according to Seegen is now further altered; it is partly converted into sugar, and at last when no further formation of sugar takes place a dextrin remains which has no reducing properties, is not further altered by ferments, which is insoluble only in very strong alcohol, and is converted into sugar by the action of acids, only when heated in sealed tubes. Thus on account of its very pronounced resistance to the action of ferments and acids Seegen has given it the name of *dystropodextrin*.

The ultimate conclusions which Seegen arrives at are, that at the end of the fermentation only 60 to 70 per cent. of the glycogen is converted into sugar by saliva or pancreas extract, and that the sugar formed is not dextrose, as it possesses a much smaller reducing power and a higher specific rotatory power. Diastase acts in a similar manner. By the same ferment starch is converted not into dextrose, but into a sugar possessing the same properties as that formed from glycogen, a sugar which he calls ferment sugar. When boiled with acids (HCl or H_2SO_4), even then only about 75 per cent. of the glycogen is converted into sugar, but in this case it appears to be dextrose which is formed. A *complete* change of glycogen into sugar takes place only when it is heated with acids in sealed tubes for 36–48 hours in a water-bath at 100°C.

The sugar formed from glycogen in the liver, however, appears to be dextrose, and inasmuch as the author was unable to extract any ferment from the liver, possessed of diastatic properties, other than a minimal action, he thinks it quite probable that the formation of sugar in the liver does not depend upon ferment action. It would now appear that while the results of Nasse and Seegen are in the main correct, and in reality substantiate the results of Musculus and Mering, their conclusions are vitiated by the manifest impurity of the so-called ptyalose and ferment sugar. Seegen's ferment sugar is, as pointed out by Musculus,[1] not a chemical individual, but is undoubtedly like Nasse's ptyalose, a mixture of maltose and dextrin with possibly a trace of dextrose. The properties assigned by Nasse and Seegen to their products are quite in accord with the results of Musculus and Mering; a combination of maltose with dextrin and a trace of dextrose would naturally give a higher specific rotatory power and less reducing power than dextrose.

[1] Zeitschrift f. Physiolog. Chem. **4**, 94, 1880.

The question has been raised recently in studying the action of ptyalin on glycogen, whether the glycogen obtained from the liver of an animal fed exclusively on carbohydrate food differs from the glycogen obtained from the liver of an animal fed on a purely albuminous diet. Schtscherbackoff[1] claimed to have demonstrated the existence of four distinct kinds of glycogen, for by boiling glycogen prepared from the liver of a dog fed on a mixed diet, with exceedingly dilute acids, he obtained four products characterized by specific rotatory power, reaction with iodine and with Fehling's solution. Seegen has likewise held it possible that liver glycogen may show a different resistance to those ferments which convert it into sugar, according as it has its origin from carbohydrates or albuminoids. But in 1877, Mering[2] attempted to show that these statements were incorrect and that only one glycogen is formed from different feedings, whether albuminous or carbohydrate, which reacts towards ferment, saliva, diastase, etc., in the same way. This idea is now substantiated by the fact that Musculus and Mering[3] have obtained from glycogen prepared by fibrin feeding and from amylaceous feeding, the same decomposition products.

According to the view generally accepted, human parotid saliva reacts more strongly alkaline than the saliva of other glands, but Astaschewsky,[4] who has lately investigated the question, has arrived at different results. He collected saliva from 16 different persons by means of fine glass tubes inserted into the ducts, and caused a flow of the secretion either by irritating the mucous membrane with ether vapor or by the mechanical act of chewing. The fresh saliva appeared thin fluid and showed no action whatever on turmeric paper, but on litmus gave an amphichromatic reaction. The more intensely the mucous membrane of the mouth is irritated the weaker becomes the acid reaction and the more rapidly appears the alkaline reaction upon violet or reddened litmus. The maximum of the diastatic action of parotid saliva corresponds with the strongest acid action. If the saliva is allowed to stand exposed to the air in open dishes, even in the cold, it becomes after a short time more or less turbid and no longer colors litmus red. Thus it appears that the fresh parotid saliva owes its acidity to the presence of carbonic acid or acid carbonates. It is further probable that the parotid saliva takes on its acid reaction first in the salivary tubes, as by very rapid secretion this reaction disappears, only to reappear again, however, after a short time.

Rapidity of Conversion of Starch into Sugar.—L. Solera[5] has attempted to answer the question how rapidly and in what quantities does human mixed saliva convert starch into sugar. By means of Fehling's solution he finds that at a temperature of 10–12°C the first traces of sugar appear in 12 seconds. On the other hand, he finds it takes a comparatively long time to convert the last residue of

[1] Ber. d. deutsch. chem. Gesell. **3**, 200. [2] Pflügers Archiv. **14**.
[3] Zeitschrift für Physiolog. Chem. **2**, 418. [4] Centralblatt f. d. med. Wissensch, 1878, **15**.
[5] Jahresbericht u. d. Fortschritte d. Thierchemie, 1879, 235.

the starch into sugar, for even after 20 hours a trace of unaltered starch can still be detected in the mixture, which, however, after 24 hours wholly disappears. If the mixture is composed of equal parts by weight of saliva and starch, or two parts of saliva to one of starch, suitably diluted with water, the starch entirely disappears in 14 hours.

On raising the temperature the rapidity of conversion is increased, thus at 35–40°C the last trace of starch entirely disappeared in 2½ hours from a mixture composed of equal parts of starch and saliva. A higher temperature (70°C) gives no increase.

Solera has also studied the behavior of different varieties of starch to saliva, viz. wheat, maize, rice and potato starch, and he finds that equal parts by weight of these different varieties of starch are not changed into equal parts by weight of sugar, and also that the conversion of the starch into sugar follows much more rapidly with certain kinds than with others; thus maize starch unites with proportionately the greatest rapidity of conversion the greatest absolute sugar production. Wheat and rice starch give ultimately equal quantities of sugar, although in different times, the wheat starch undergoes the change most rapidly, while potato starch which is changed quite rapidly into sugar yields the smallest absolute quantity.

Action of Saliva in the Stomach.—Various results have been obtained by different experimenters in studying the action of saliva in the stomach. This is naturally a very important question, since the mixture of amylaceous food and saliva is almost immediately carried into the acid gastric juice, where a possibly antagonistic ferment is active in a distinctly acid medium. A slight alteration of the reaction of saliva does not appear to destroy its diastatic action; thus, according to the experiments of Paschutin and Lehmann. as well as of others, the addition of very small quantities of alkali and acids have no influence on the alteration of starch by saliva, while, according to W. H. Watson,[1] the addition of very minute quantities of hydrochloric acid appears to increase the diastatic action. In solutions containing .2 per cent. of hydrochloric acid the diastatic action of saliva wholly ceases. Reinhard v. d. Velden[2] has, however, recently studied the character of gastric juice, taken by means of a pump from healthy human stomachs in different stages of digestion. He finds that, in the first stage of digestion, when the gastric juice is already strongly acid, free hydrochloric acid cannot be detected by fuchsine, methyaniline violet, etc. The time at which the hydrochloric acid can first be detected varies in different individuals, and appears in mixed diet to be dependent upon the quantity of food taken. Thus, after breakfast consisting of tea, bread and meat, the hydrochloric acid did not appear until ¾—1 hour, while after a complete dinner not until 2 hours. In gastric juice taken from the stomach soon, but not too soon, after

[1] Jour. Chem. Soc. 1879, 539. [2] Zeitschrift für physiolog. Chem. 3, 205.

meal time, a solution of iodine in potassium iodide always gave a wine yellow color. Reinhard v. d. Velden also found that if starch paste and fresh human saliva were added to gastric juice in which the acidity was not due to hydrochloric acid, iodine gave only a bright yellow color. If, on the other hand, gastric juice containing hydrochloric acid was taken, iodine always showed a blue color, even when a large quantity of saliva was added and the test allowed to stand for a long time at 40° C. Thus it would appear that in the stomach there are two stages of digestion, separable one from the other—a first, in which the action of saliva can go on without hindrance, and a second, in which the pepsin alone is active; a stage of amylaceous and a stage of proteid digestion.

R. H. CHITTENDEN.

REPORT ON ANALYTICAL CHEMISTRY.

[*Continued from p. 71.*]

ZINC.—*Separation from Cadmium.*—A. Yver.[1] The solution containing the two metals as acetates is treated with two or three grams of acetate of sodium and a few drops of acetic acid and then subjected to electrolysis. The battery used consists of two Daniell's cells of the usual form. The cadmium is completely precipitated upon the negative pole, while all of the zinc remains in solution. The deposition takes place in the cold and is complete within three or four hours, when the quantities of the metals range between 0.180 and 0.210 gram.

Separation from Copper.—G. Larsen.[2] A single precipitation with sulphide of hydrogen suffices for a complete separation of the two metals, provided the solution is acid with hydrochloric acid and hot when treated with the gas, and the precipitate is washed with a hot solution of sulphide of hydrogen containing hydrochloric acid.

CADMIUM.—*Separation from Copper.*—G. Vortmann.[3] The dilute solution is treated with hyposulphite of sodium until it becomes colorless, and then heated to the boiling point. The copper precipitates as sulphide.

SILVER.—*Electrolytic Deposition.*—H. Fresenius and F. Bergmann.[4] The tendency of silver to precipitate in a spongy or flocculent condition when deposited from an acid solution by electrolysis can be avoided by employing a weak current and dilute solution. The following conditions were found to be the most satisfactory: A solution containing in 200 cc. from 0.03 to 0.04 gram of silver and from 3 to 6 grams of nitric acid; a separation of the electrodes of one centimeter; a current sufficient to yield

[1] Bull. de la Soc. Chim. **34**, 18.
[2] Dingler's Jour. **239**, 239.
[3] Monatshefte für Chemie, **1**, 952.
[4] Zeitsch. f. analyt. Ch. 1880, 324.

from 100 to 150 cc. of electrolytic gas per hour. From a dilute neutral solution the silver deposits in a flocculent condition however weak the current.

Separation from Lead.—E. Donath.[1] The solution is treated with 4 or 5 cc. of glycerine, an excess of ammonia, and finally with 10 or 15 cc. of concentrated caustic potassa or soda. Complete solution ensues. The whole is then boiled four or five minutes, with constant stirring. Lead, also bismuth and copper, remains in solution, while the silver is completely precipitated as metal. The precipitate is washed with hot water, then with hot dilute acetic acid, and finally with hot water again. The washing with acetic acid is necessary in order to remove any carbonate of lead which may have formed in the filter during the first washing with water.

MERCURY.—*Detection in Dilute Solutions.*—J. Lefort.[2] It was shown by Orfila that the gold-tin voltaic couple of Smithson, devised for the detection of minute quantities of mercury, might lead to erroneous conclusions in consequence of the deposition of a portion of the tin upon the gold. It is, however, easy to distinguish a deposit of mercury from one of tin, since by placing the strip of gold foil in a narrow glass tube and heating, the former is readily sublimed, and its presence can be confirmed by exposing the sublimate to the vapors of iodine. A more curious difficulty presents itself when the solution to be examined contains arsenic. The couple reduces the compounds of arsenic quite readily with precipitation, first upon the tin and then upon the gold. When the latter is heated the arsenic sublimes, and cannot be easily distinguished in the sublimate from mercury, especially since the vapors of iodine convert it into a compound whose color resembles that of the iodide of mercury. This chance of mistaking arsenic for mercury should not be lost sight of when defective analyses are seemingly establishing the wide diffusion of mercury in mineral waters.

NICKEL AND COBALT.—H. Fresenius and F. Bergmann[3] have undertaken to ascertain the conditions most favorable for the electrolytic deposition of nickel and cobalt. They recommend for both a solution containing in 200 cc. from 0.1 to 0.15 gram of the metal as sulphate, from 2.5 to 4.0 grams of ammonia (NH_3), and from 6 to 9 grams of sulphate of ammonium; a current equivalent to 300 cc. of electrolytic gas per hour, and a separation of $\frac{1}{3}$ or $\frac{1}{2}$ cm. for the electrodes. If less ammonia is used the results are not good. Larger quantities retard the deposition, but do no further harm.

Qualitative Separation of Nickel and Cobalt.—F. Reichel.[4] Both metals are precipitated by caustic potassa. The precipitate, filtered but not washed, is placed in a test tube. A piece of solid

[1] Monatshefte für Chemie, **1**, 789.
[2] Compt. Rend. **90**, 141.
[3] Zeitsch. an. Ch. 1880, 314.
[4] Zeitsch. an. Ch. 1880, 468.

potassium hydroxide and just enough water to dissolve it are added. On boiling the cobalt dissolves, and imparts a blue color to the solution. In this way minute quantities of cobalt can be expeditiously detected.

IRON.—*Precipitation by Succinate of Ammonium.*[1]—The statement of Fresenius that the precipitate of iron by succinate of ammonium is partially redissolved by heating has been found to be incorrect. The filtrate contains less iron than when the precipitation has been effected in the cold. Hot succinic acid dissolves very little of the precipitate, whether the precipitation has been effected in hot or cold solutions, but more in the latter than in the former case. Cold succinic acid dissolves more than hot. It is therefore recommended to precipitate from hot solutions and to boil two or three minutes before filtering.

ALUMINUM.—*Separation from Iron.*—E. Donath.[2] The neutral or slightly acid solution is treated with hyposulphite of sodium until all ferric compounds have been reduced. A solution of cyanide of potassium having twice the volume of the iron-aluminum solution, and containing from 15 to 20 grams of cyanide of potassium, is heated to boiling, and the iron-aluminum solution slowly poured into it. The solution is then quickly cooled, acidified with acetic acid, and the aluminum precipitated with carbonate of ammonium. If the aluminum hydroxide has not a pure white color, it must be dissolved and reprecipitated. The separation is quantitative.

MANGANESE.—*Use of Permanganate in Presence of Hydrochloric Acid.*—C. Zimmermann.[3] The usefulness of permanganate of potassium in volumetric analysis is considerably diminished by the fact that it cannot be used in solutions containing hydrochloric acid. The author has discovered that, by adding manganous sulphate, this difficulty can be wholly obviated. The solution in which the titration is to be made must, however, contain no free sulphuric acid.

Quantitative Determinations by Potassium Permanganate in Alkaline Solution.—E. Donath.[4] Hitherto this compound has been employed only in neutral or acid solution. Preliminary experiments, however, indicate that it can be successfully used in alkaline solution for the determination of both chromium and manganese. The reactions supposed to take place are as follows:

$$Mn_2O_7 + Cr_2O_3 = 2CrO_3 + MnO_2$$
$$3MnO + Mn_2O_7 = 5MnO_2$$

The standard solution of permanganate is rendered alkaline by addition of sodium carbonate and caustic soda, and heated nearly to boiling. The neutral solution of the chromous or manganous compound is then allowed to flow in until complete reduction of the permanganate has been effected.

H. N. MORSE.

[1] Jour. Chem. Soc. 1880, 674.
[2] Monatshefte für Chemie, **1**, 785.
[3] Berichte d. deutsch. chem. Gesellsch. 1881, 779.
[4] Berichte d. deutsch. ch. Gesellsch. 1881, 982.

NOTES.

Note to paper "Alkalimetry with Phenol Phthalein as Indicator."

A recent article on the subject mentioned in the title was prepared for this Journal before I had read Lux's paper on "Flavescin;"[1] otherwise I should have made the proper acknowledgment at that time of his priority in the general method of distinguishing alkalinity and causticity by an indicator which is indifferent to alkaline bicarbonates.

R. B. WARDER.

Precipitation of Ammonium Phospho-molybdate in presence of Salts of Organic Acids.

In Fresenius' standard treatise on quantitative analysis appears the sentence: "Weinsäure und ähnliche organische substanzen verhindern die Fällung des phosphorsäuren Molybdänsäure Ammons ganz und gar (Eggertz)." This statement is certainly too strongly worded.

In a recent experiment one portion of the solution obtained by exhausting a "super-phosphate" with water and then digesting with solution of ammonium citrate (sp. g. = 1.09) was evaporated to dryness, the residue very carefully burned, redissolved with the aid of a little nitric acid, and ammonium molybdate with nitric acid in excess added as usual. A second portion of the same solution was treated directly with a large excess of strong nitric acid, and the ammonium molybdate added at once. There was no escape of gas or other sign of violent action on the citrate, which had been used to the full extent recommended by Fresenius, Neubaum and Luck.

The first portion gave 2.69 per cent.
The second portion gave 2.56 per cent.

of P_2O_5 on the superphosphate taken.

Hence the presence of ammonium citrate in large quantity only caused a loss of 4.83 per cent. on the P_2O_5 actually present; enough, of course, to make it necessary to burn off the organic matter, but clearly contradicting the last words of the sentence quoted above.

J. W. MALLET.

[1] Zeitsch. anal. Chem. **19**, 457.